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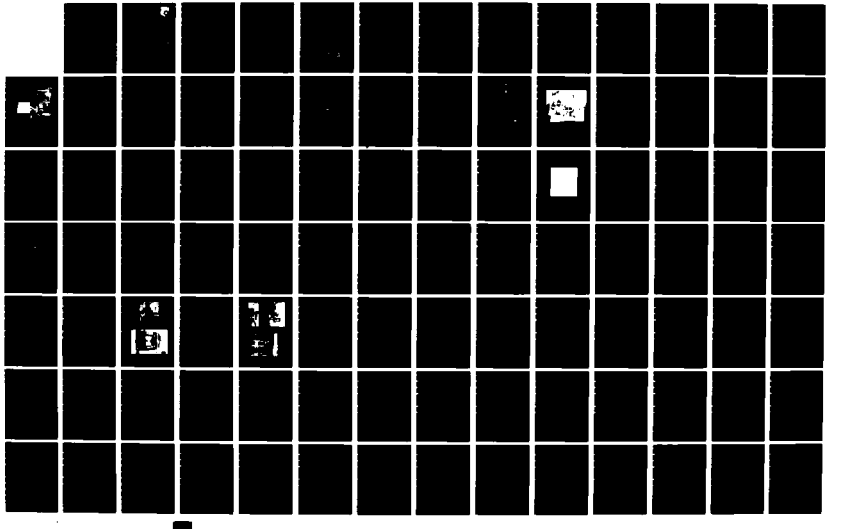

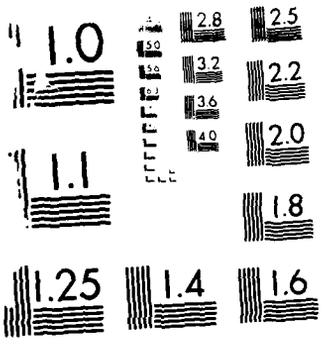

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AFWAL-TR-85-2043

DEVELOPMENT OF A PORTABLE WEAR METAL ANALYZER FOR FIELD USE

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August 1985

Final Report for Period August 1982 - August 1985

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This technical report has been reviewed and is approved for publication.

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The portable wear metal analyzer (PWMA) was developed for the USAF to perform engine oil analysis when aircraft are deployed away from their home bases. The analyzer can detect nine wear metals in the parts per million concentration ranges. The analyzer utilizes the graphite furnace atomic absorption technology with a specially developed multi-element analysis scheme. The overall system is packaged into two militarized suitcases, including a nine-channel spectrometer, an air or water-cooled graphite furnace, a miniaturized graphite furnace power supply, a unique sample introduction device, a pneumatic supply

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20. ABSTRACT (continued)

system, and microprocessor controlled electronics. The analyzer is simple to set up and use. The operator only needs to introduce an undiluted oil sample, push a start button and wait for the results to be printed out.

A brassboard system was first developed followed by six prototypes. Analytical performance as well as environmental compatibility were thoroughly evaluated on the first prototype. Consequently, design improvements were made and incorporated into five subsequent prototypes.

Test results of the prototypes indicated that the instrument can meet the oil analysis need in both laboratory and rugged environments. Field tests are under way and the results will further verify the validity of the instrument.

PREFACE

The Portable Wear Metal Analyzer (PWMA) program has been conducted by the Perkin-Elmer Corporation, Applied Science Division at Pomona, California. The instrument can analyze nine trace metals commonly found in aircraft engine oil and is intended to provide the required oil analysis data for the USAF aircraft during deployment. The instrument is based on graphite furnace atomic absorption technology with a specially developed multi-element analysis scheme. As a result of this development, six prototypes were constructed and delivered for field evaluation. This report describes major design features, the analytical performance, and the environmental compatibility of the instrument.

The PWMA developed under this program has demonstrated the capability of meeting the needs for oil analysis during deployment. The multi-element approach developed is a new instrument concept and is the only one of its kind. Major achievements include:

a. Developed a multi-element analysis scheme to analyze nine elements in one oil sample.

b. Developed a miniaturized graphite furnace power supply capable of delivering 500 amperes along with an air or water cooled graphite furnace.

c. Developed a novel, simple, and highly repeatable sample introduction device.

d. Designed a compact nine channel spectrometer with high thermal stability.

e. Packaged the instrument in a portable and ruggedized version with a simple one-pushbutton operation.

During the progress of the development, areas of improvement have also been identified. To further improve the manufacturability and the accuracy of the instrument, the following recommendations are suggested and detailed in Chapters 7 and 9:

a. Use only 220 V ac for the power source to reduce the complication of high current switching between 220 V and 110 V.

b. Select either water or air for cooling the graphite furnace to facilitate the design improvement of cooling efficiency and speed.

c. Reassess the working ranges required for aircraft oil analysis so that the calibration of the instrument can be focused on most commonly used ranges, thus improving the accuracy within these ranges.

d. Analyze silicon in a separate run. Since silicon analysis is not presently required for most of the aircraft, this separation will allow optimization of the atomization cycle, thus improving the performance of other elements.

e. Reduce the operating temperature specification from -18 to 57 degrees centigrade to 0 to 50 degrees centigrade. This temperature reduction will simplify the component selection constraint, thus reducing the manufacturing cost.

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CHAPTER I
INTRODUCTION

1.1 SCOPE

This final report describes Perkin-Elmer Corporation development efforts on the Portable Wear Metal Analyzer (PWMA) and the performance of prototype units which are shown in Figure 1. The report covers the period from August 1982 to August 1985.

1.2 BACKGROUND

1.2.1 SPECTROMETRIC OIL ANALYSIS PROGRAM

Modern spectrometric methods have been routinely used to detect trace metals in aircraft engine lubricating oil as an indication of service condition. Wear metal particles are generated by relative motion between the contact area of metallic parts. The metal particles entering the surrounding lubricant can be detected and quantified by spectrometric methods. A large amount of wear metal data has been collected; wearing trends have been used to predict engine conditions. An abnormal wear rate can be related to the probable source within the engine and appropriate maintenance action can be taken before failure occurs. The value of the Department of Defense (DoD) Joint Oil Analysis Program (JOAP) has been proven over the past two decades. Presently, the United States Air Force has over 100 JOAP laboratories throughout the world, and over 1.5 million samples are analyzed yearly.

1.2.2 THE PORTABLE WEAR METAL ANALYZER

When USAF aircraft are deployed away from their home bases, the requirement for engine oil analysis still exists. Due to the critical nature of aircraft turbine engines, some aircraft are required to have engine oil analyzed after each flight. Laboratory-type Flame Atomic Absorption (FAA) spectrometers have been used for deployment support with limited success. The requirement for using nitrous oxide/acetylene gases and methyl isobutyl ketone solvent makes the FAA

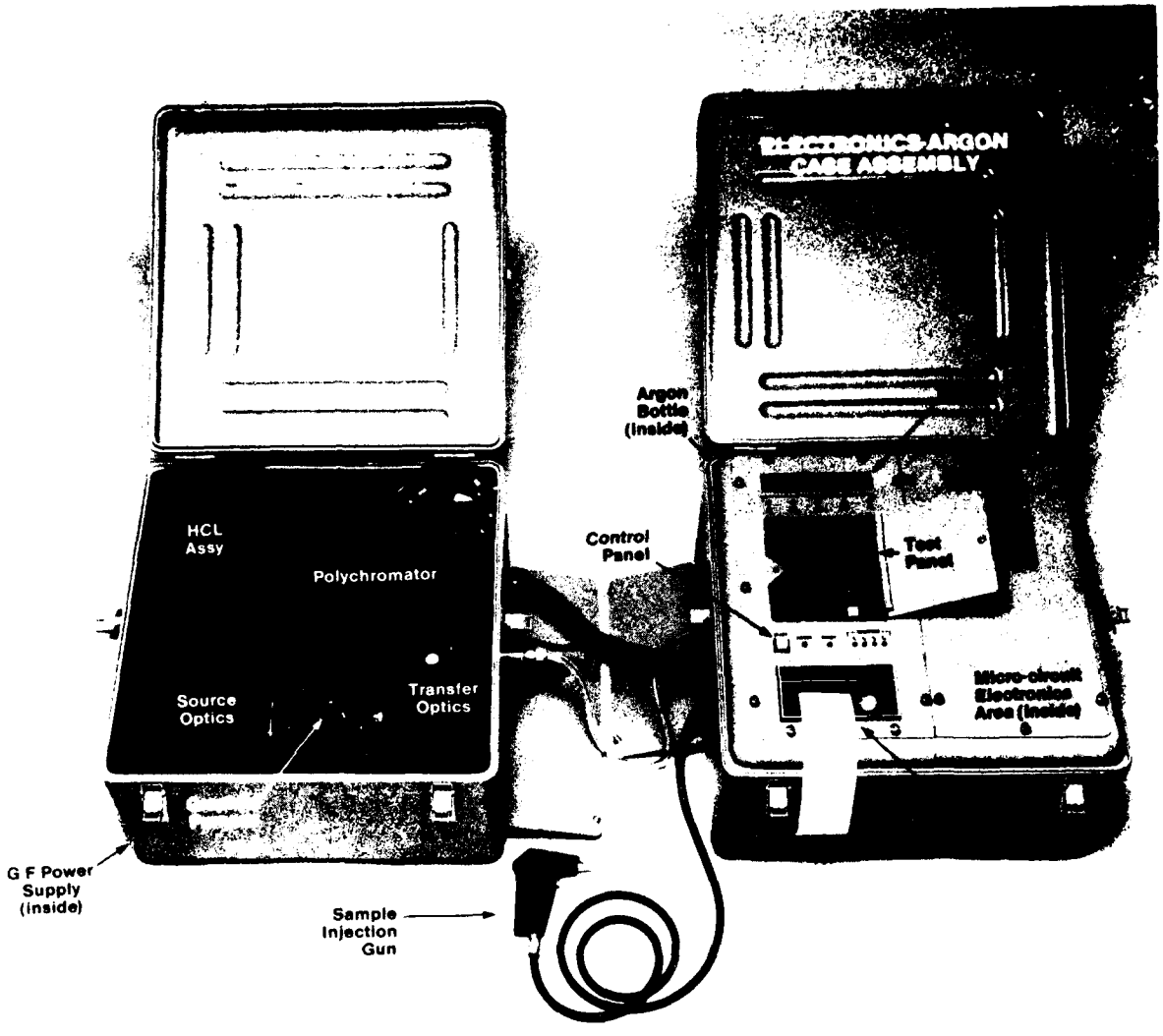

FIGURE 1. The Portable Wear Metal Analyzer

technique undesirable for field use. The logistics involved in moving the various supplies, associated with this technique, are extremely difficult and costly. Furthermore, the FAA spectrometer is operated on a one-element-at-a-time basis; thus, the measuring of nine elements is cumbersome and time consuming. It is critical, therefore, that a portable, easy to operate, and reliable system be developed to perform oil analyses during aircraft deployment.

1.2.3 PORTABLE WEAR METAL ANALYZER DEVELOPMENT

In October 1981, the USAF funded a feasibility study to determine the techniques suitable for a PWMA[1]. Techniques under consideration included atomic emission spectroscopy, atomic absorption spectroscopy, X-ray fluorescence spectroscopy, colorimetry, and radioactive tagging. The study concluded that Graphite Furnace Atomic Absorption (GFAA) spectroscopy is the best technique for a PWMA application.

Based on this study, the USAF funded a contract to Perkin-Elmer Corporation to develop a PWMA using graphite furnace AA technology. The PWMA design objectives are described below.

a. Multi-element Analysis. The PWMA shall be capable of analyzing engine lubricating oil for Silver (Ag), Aluminum (Al), Chromium (Cr), Copper (Cu), Iron (Fe), Magnesium (Mg), Nickel (Ni), Silicon (Si), and Titanium (Ti), within the concentration ranges listed below:

Ag (1-10 ppm)	Cu (1-40 ppm)	Ni (1-30 ppm)
Al (1-50 ppm)	Fe (1-100 ppm)	Si (1-20 ppm)
Cr (1-10 ppm)	Mg (1-50 ppm)	Ti (1-20 ppm)

Measurement repeatability should be within ±1 ppm or ±2.5% of the full scale, whichever is greater.

b. Two-Suitcase Portability. The PWMA shall be packaged in two containers balanced for one-man portability.

c. Field Operation. The PWMA shall be capable of field setup and operation requiring only line power of 115/230 volts alternating current (VAC), 50-60 cycles per second (Hz).

d. Environmental Protection. The PWMA shall be designed for operation under the following conditions:

1. Shock - withstand 30 gravity (g) loads

2. Temperature

Storage: -55 to +70° Centigrade (°C)

Operation: -18 to +57°C

3. Humidity: 0 to 100% with no condensation

4. Altitude:

Storage: -250 feet to 25,000 feet

Operation: -250 feet to 15,000 feet

e. Simplified "One-Button" Operation. The PWMA shall be designed for operation by flight line personnel having minimum training in JOAP procedures.

f. Self-Contained Operation and Consumables. The PWMA shall be capable of self-contained operation and provide adequate supply and storage of consumables.

g. Correlation with JOAP Data Bases. The PWMA shall produce results consistent with existing JOAP data bases. Because of greater particle size independence, the PWMA wear metal data will be more accurate than wear metal data collected from other JOAP instruments.

h. Calibration Standard. The PWMA shall be calibrated using organometallic standards in MIL-L-6082, Grade 1100 oil (reference Paragraph 4.2).

i. Oil Sample Composition. The PWMA shall analyze wear metal samples in MIL-L-23699 and MIL-L-7808 engine lubricating oils.

1.3 MULTI-ELEMENT ATOMIC ABSORPTION ANALYSIS

1.3.1 ATOMIC ABSORPTION

The atomic absorption analysis relies on the principle that an atom can absorb specific energy and change the atom's electronic configuration. The atom is made of a nucleus surrounded by electrons. Every element has a specific number of electrons that are associated with the atomic nucleus in an orbital structure that is unique to each element. The lowest energy, or most stable electronic configuration of an atom, known as the "ground state", is the normal orbital structure of an atom. If energy of the right magnitude is applied to an atom, the energy will be absorbed by the atom and an outer electron will be promoted to a less stable configuration or "excited state."

In most commercial AA instruments, a single-element hollow cathode lamp (HCL) is used as the light source for emitting energy. The cathode of the HCL is made of an element that is the element to be measured. Thus, the discrete energies (wavelengths) emitted by the HCL correspond to the energies required to promote the outer electron of that element from the ground state to different excited states. The absorption signals can be measured by a photomultiplier detector, which senses the reduced light level when the absorption occurs. Usually, a monochromator is employed to isolate unwanted radiations originated from the HCL, and an atomizer is used to atomize the element in the sample.

To analyze wear metals in oil, an oil specimen is sampled and presented to the atomizer. Wear metals are then atomized and the absorption signals measured can be related to the wear metal concentrations through proper calibration. Two types of atomizers can be used for oil analysis: One type is a flame atomizer where mixtures of air-acetylene or nitrous oxide-acetylene are used as fuel. The oil sample diluted in organic solvents is aspirated through a nebulizer and atomized in the flame. Another type of atomizer is a graphite furnace where a high current is passed through a graphite tube and the electric resistance heating generated in the tube is used to atomize the oil sample. For logistic reasons, the graphite furnace atomizer was selected for the PWMA.

1.3.2 MULTI-ELEMENT ANALYSIS

Commercial AA spectrometers are essentially designed for single element detection. To measure successive elements, the HCL, the monochromator setting, and the atomization condition usually need to be changed. Modern instruments use microcomputers to control these parameters and to perform sequential multi-element analyses; however, a new sample must be introduced for each analysis. Recently, a multi-element AA instrument was reported [2], however, it is not yet commercially available.

To meet the multi-element requirement of the PWMA, two multi-element HCLs are used wherein one lamp contains six elements and the other lamp contains three elements. The two lamps are operated alternately. A nine channel polychromator with nine individual detectors is employed. Each channel corresponds to one spectral absorption line in order to detect each of the nine wear metals in one atomization cycle. The atomization condition for each element was tested individually and a programmed atomization cycle was developed to accommodate all elements to be analyzed. The atomization cycle is discussed in Chapter III.

As described in the previous section, the element in the HCL matches the element to be measured, thus high specificity is obtained. For multi-element detection, only emission lines from different elements in the same lamp need to be separated; the spectral bandwidth requirement for the polychromator ranges from 0.1 to 1 nm for the PWMA. This resolution is less stringent than those of the atomic emission instrument where emissions from all the metals presented in the oil sample need to be isolated. Furthermore, the AA signal is derived from the ratio of the light intensities before and after atomic absorption. Thus, the signal is less susceptible to absolute spectra intensity variation caused by environmental conditions. The inherent nature of AA spectroscopy is the main reason for developing a graphite furnace AA for the PWMA.

1.4 PORTABILITY

Setup and operation of the PWMA is illustrated in Figure 2. Emphasis has been placed on field operation and portability since these are the principal requirements of the PWMA. The PWMA is packaged into two military-grade containers.

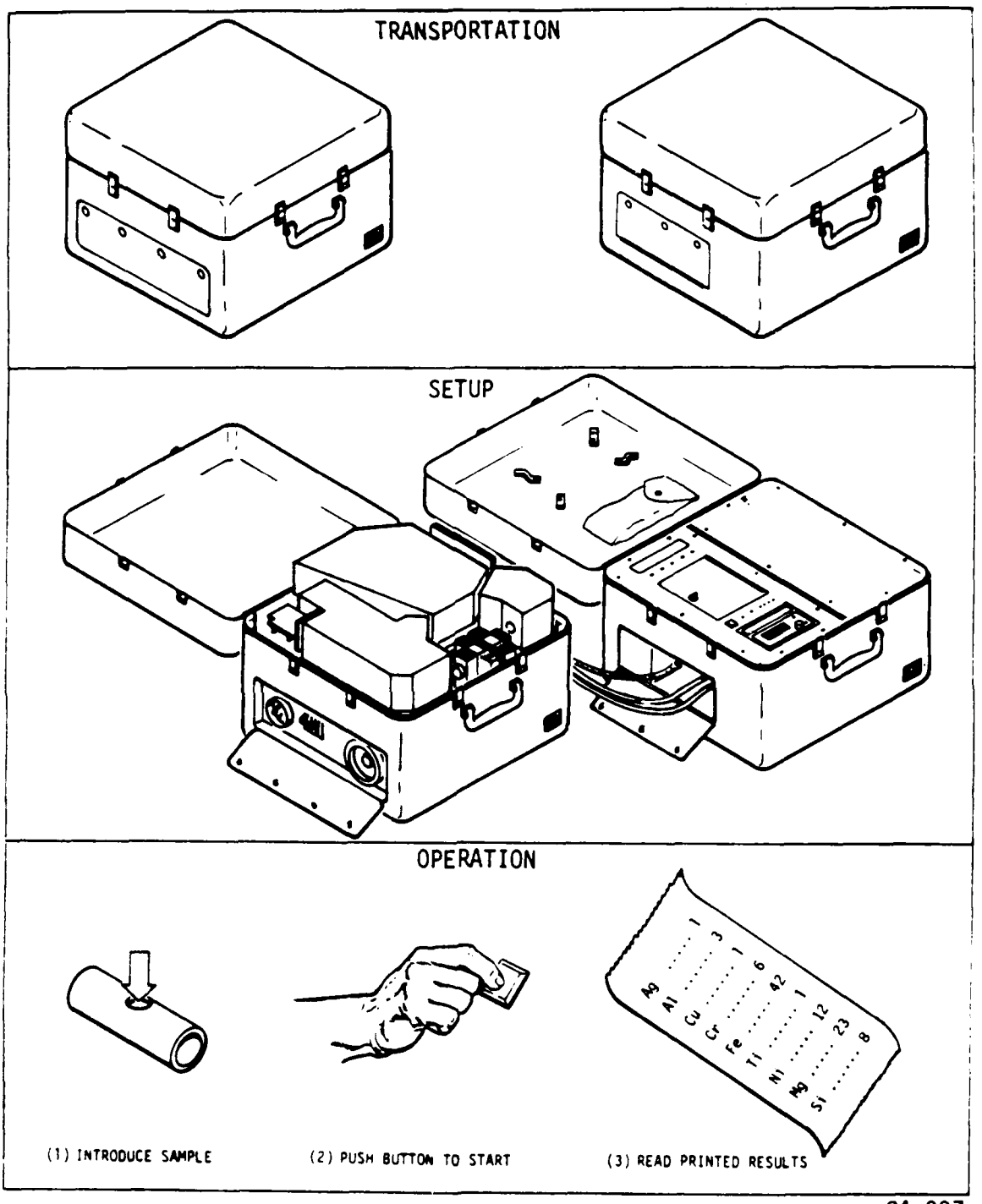

FIGURE 2. PWMA System Setup and Operation

One container weighs 40 pounds and the other weighs 60 pounds. Both are designed to provide full environmental protection for storage and transportation. The PWMA is quickly set up by placing the two containers side-by-side, making the necessary connections, and turning the instrument on. The PWMA provides self-contained operation using air cooling and a built-in argon gas supply. The only external requirement is electrical power service at 115/230 VAC, 50-60 Hz.

The PWMA has simple "one-button" operation under preprogrammed microcomputer control; thus, only minimum operator skill and training are required and the opportunity for operator error is reduced. The analyzer accepts undiluted oil samples to eliminate errors due to solvent-dilution procedures and to simplify instrument operation.

CHAPTER II
PWMA SYSTEM

2.1 SYSTEM DESCRIPTION

A block diagram representation of the PWMA oil analysis sequence is shown in Figure 3. The operator first introduces an oil sample into the graphite tube of the Graphite Furnace Assembly. The PWMA start button, located on the control panel, is then depressed, and the entire analysis program is initiated and controlled by an "on board" microcomputer. As the graphite furnace executes the atomization cycle, the wear metals are atomized. In parallel with the atomization cycle, the emission line spectra originating from the HCLs are focused through the graphite tube to the polychromator where they are separated into individual spectral lines and are further conveyed to the exit slits. The spectral lines pass through their respective exit slits where their spectral intensities are detected and measured by individual Photomultiplier Tubes (PMTs). The presence of wear metals in the oil sample will absorb the light associated with each metal's spectral line thus reducing the intensities reaching the PMTs. The amount of light absorbed is related to the concentration of metal in the oil sample. Through proper calculation, the wear metal concentrations, in parts per million (ppm), are then calculated by PWMA microcomputers and the calculation results are then available as hardcopy printout or as individual readings on the PWMA alphanumeric display.

2.2 POLYCHROMATOR

2.2.1 DIFFRACTION GRATING

A reflecting diffraction grating is a reflective surface with evenly spaced parallel grooves. Light beams that strike the grating are reflected at angular separations dependent upon their wavelengths. A reflecting concave grating is used in the PWMA both to separate the incident beam and to focus the reflected spectrum. The spectrum is focused on a circular focal plane where nine exit slits are located. The polychromator is shown in the upper right portion of Figure 4. The use of the term "Eagle polychromator" refers to the configuration where the entrance slit and the exit slits lie on the same side of the grating normal.

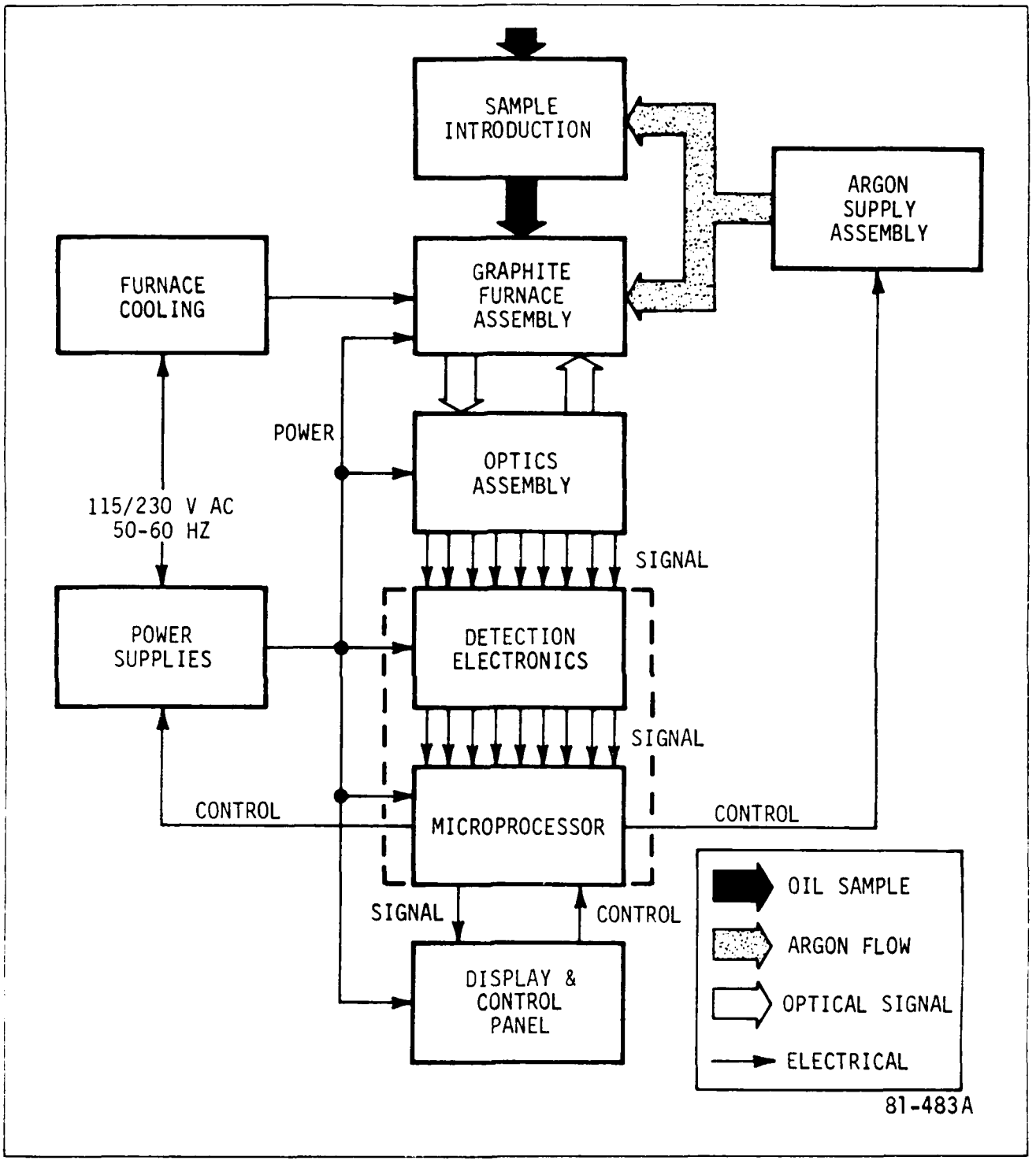

FIGURE 3. PWMA Block Diagram, Oil Analysis Sequence

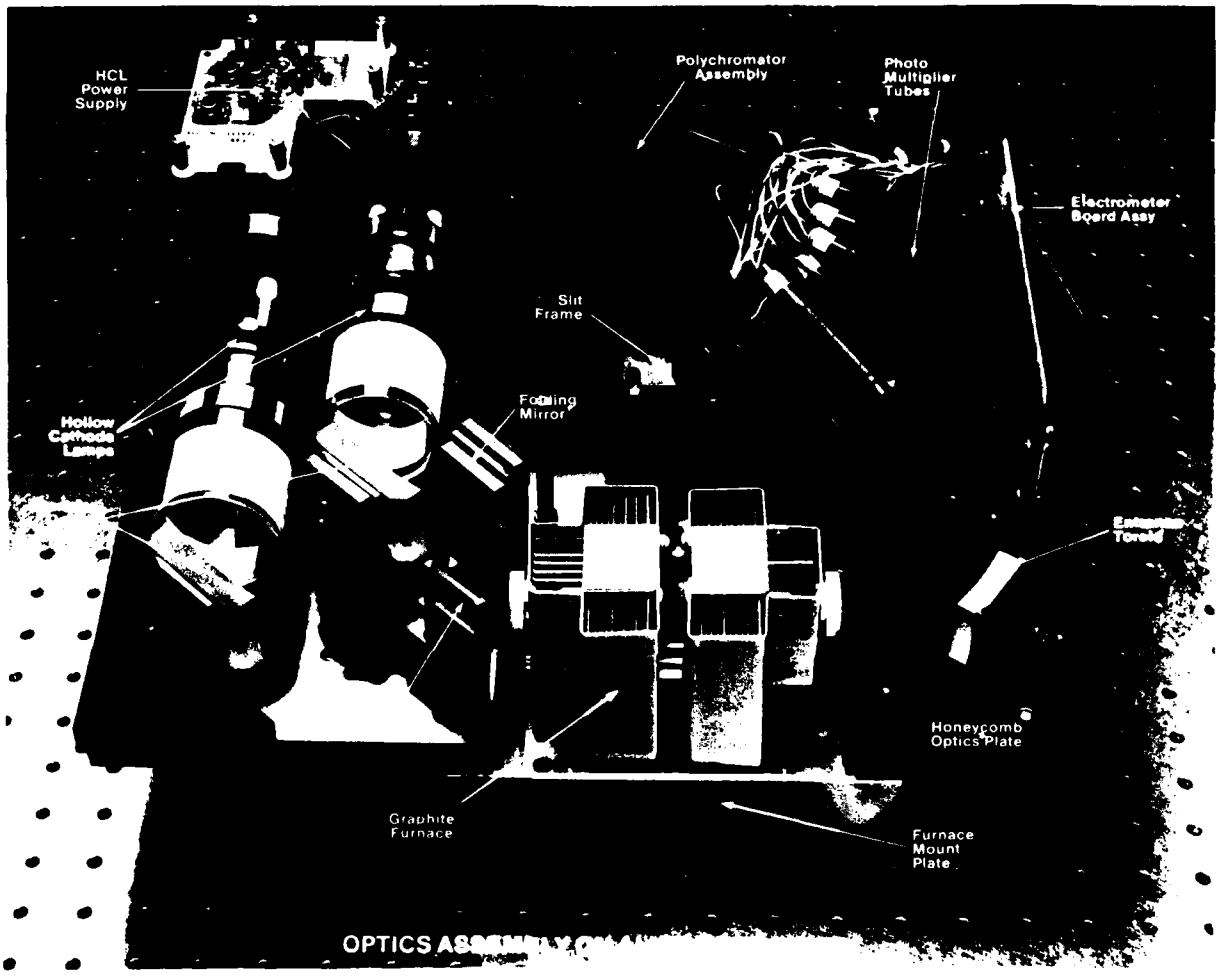

FIGURE 4. PWMA System Optics

2.2.2 DESIGN PARAMETERS

The general expression for a diffraction grating can be written as:

$$n\lambda = d\ (\sin\alpha \pm \sin\beta)$$

where n = order number

λ = wavelength

d = grating spacing, 1/number of grooves

α = angle of incidence

β = angle of diffraction

The parameter of most interest is the reciprocal linear dispersion, which gives the linear separation of spectral lines along the focal plane:

$$\text{reciprocal linear dispersion} = \frac{d \cos\beta}{nf}$$

where d = grating spacing, 1/number of grooves

β = angle of diffraction

n = order number

f = distance between the grating and focal plane

The first order spectrum (n = 1) is selected for PWMA. The spectral bandpass, which defines the practical resolution of the polychromator, is the product of the reciprocal linear dispersion and the slit width.

The quality of a polychromator is characterized by its resolution, optical speed, and image quality. Unfortunately, these three parameters are interrelated. For example, increasing the focal length improves the resolution of a polychromator. However, a longer focal length decreases the optical speed of the polychromator. A computer ray tracing program was developed to optimize these parameters. As a result, a resolution of 0.1 nm is achieved with a focal length of 20 cm where curved slits are employed to minimize aberration.

2.2.3 PACKAGE CONSIDERATIONS

Due to the space limitation, a polychromator of focal length less than 20 cm was first established as a design criteria. A short focal length, however, limits

the size of the polychromator focal plane, complicating the arrangement of the detector assembly behind each exit slit. The use of fiber optic bundles to couple the exit slits to the photomultiplier detectors was considered first; however, deep ultraviolet transmission fiber optic bundles were not available at the time of the polychromator design. The package problem was finally resolved by incorporating small mirrors to the back of the exit slits to reflect the spectral lines to their respective PMTs. By tilting the mirrors, the spectral lines may be reflected either upward or downward. Five PMTs are mounted on top of the slit frame, as shown in Figure 4, and four PMTs are located at the bottom of the slit frame (not shown).

2.3 TRANSFER OPTICS

The transfer optics focus the emission spectra through the graphite furnace tube and onto the entrance slit of the polychromator. As shown in Figure 4, the emission spectra from HCL number one is focused by the toroidal mirror to the center of the graphite tube through the beam combiner. The beam is then reflected by the spectrometer entrance toroid and focused on the entrance slit of the polychromator. The emission spectra from HCL number two is focused to the entrance slit of the polychromator in a similar path except that a folding mirror is inserted to reflect the light path for compact packaging.

The spectral range of the PWMA extends from 200 nm to 430 nm, which is mainly in the ultraviolet region. Quartz material is used for the HCL lamp envelope, the windows, and the beam combiner for maximum ultraviolet transmission. Torodial mirrors are utilized instead of spherical mirrors to minimize the astigmatism, which is significant, since relatively large off-axis angles are used in focusing the beam. The focal lengths and the angles are optimized for maximum efficiency and compactness. Finally, thermal stability, adjustability, and ruggedness are considered in the design and in the materials used for the polychromator and the transfer optics.

2.4 HEATED GRAPHITE FURNACE

2.4.1 DESCRIPTION

The graphite furnace atomizer converts wear metals in the oil sample into atomic vapors. Figure 5 illustrates the commercial furnace and the PWMA furnace. The

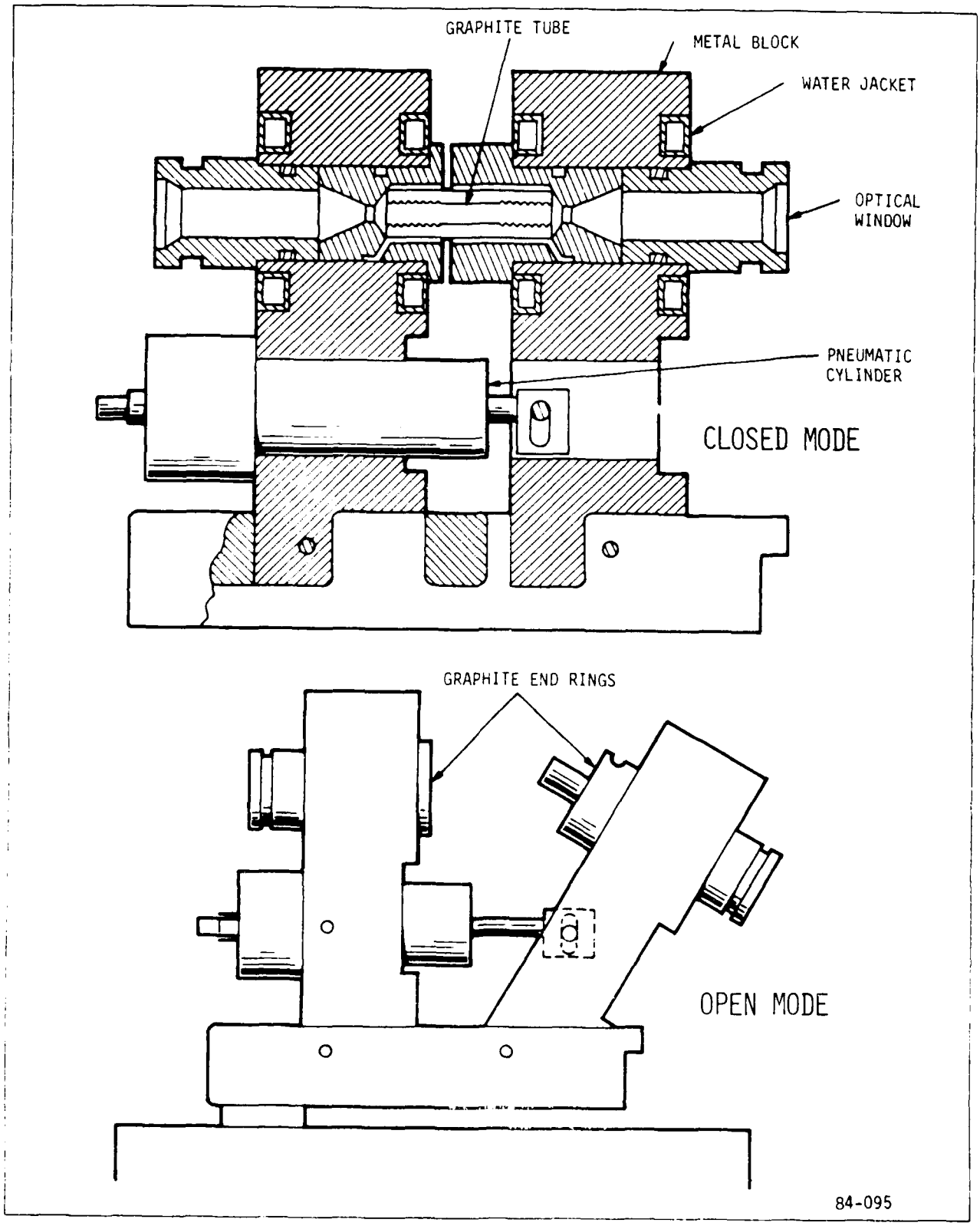

FIGURE 5a. Graphite Furnace, Cross-Sectional View

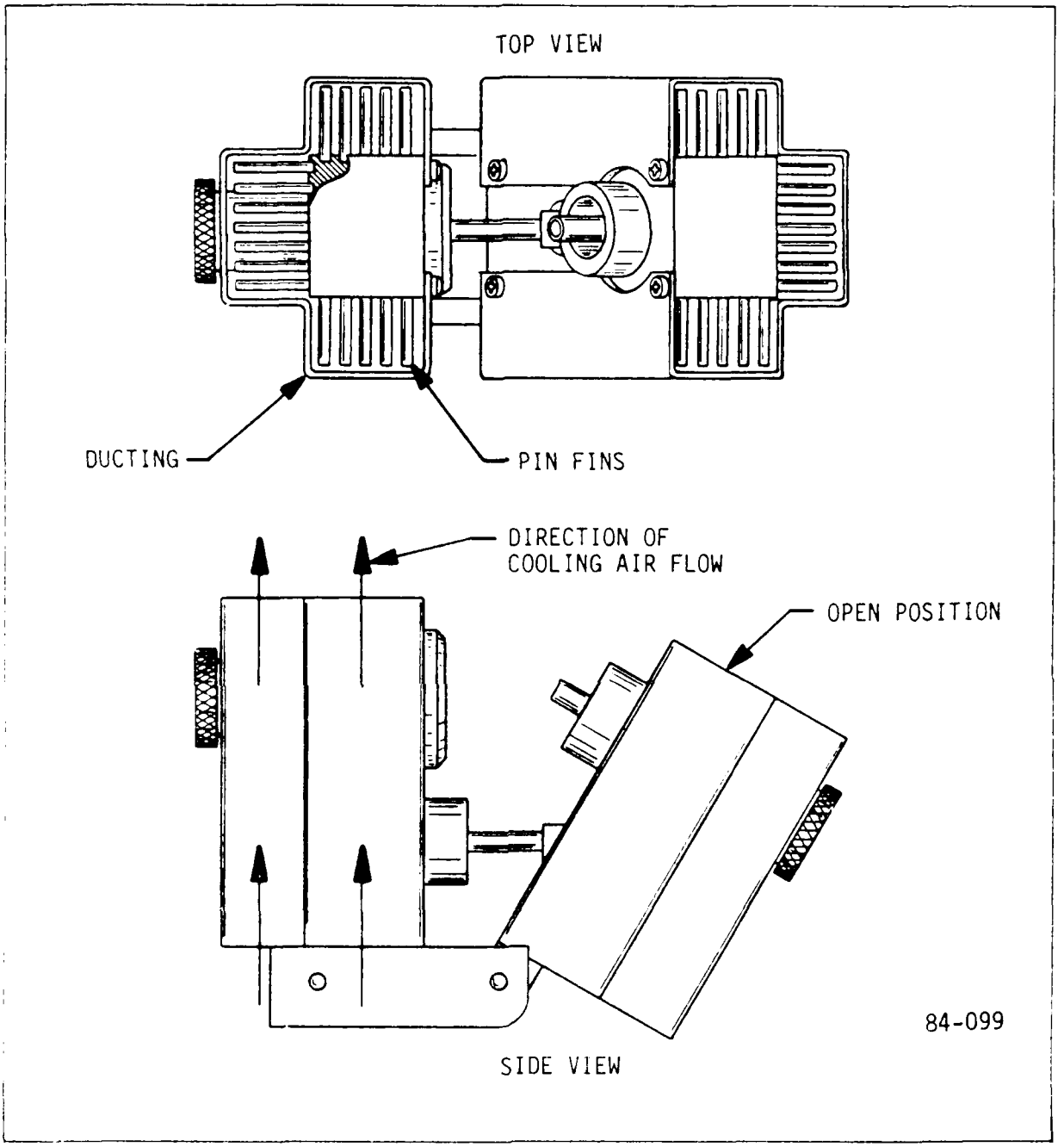

FIGURE 5b. Modified PWMA Graphite Furnace

graphite tube, which is aligned in the spectrometer optical path, is an open-ended cylinder of graphite with a small hole in the center through which the sample is introduced. The tube is held between two large graphite rings, which provide electrical contact. The graphite tube acts as a resistor in an electrical circuit. When a current is flowing through the tube, the tube can be heated to high temperatures (up to a maximum of about 3000°C). The graphite furnace is usually held by water cooled metal blocks. By circulating water through the housing, the outside temperature of the furnace is kept at a safe level. In addition, an inert gas purge of the graphite tube is required to prevent the tube from air oxidation.

2.4.2 PWMA FURNACE COOLING

For logistical reasons, the use of an air cooled furnace is highly desirable. However, water cooling is more efficient and the cooling time requirement is considerably less. The PWMA furnace can be used in either cooling mode. Approximately 500 beryllium-copper pins, 3/32 inch diameter, are press-fit into the metal blocks of the furnace. A cooling fan is mounted at the base of the furnace. The pins provide an efficient heat sink without obstructing the open/close operation of the furnace or the cooling water pipe system. This pin fin design is superior to conventional heat sink designs because the configuration enhances the turbulent flow of air through the pins and the press fit provides better heat conduction than the use of thermal epoxy to bond a heat sink to the metal blocks. A computer model was developed to calculate heat dissipation of the pins. The model showed that given the designed atomization cycle, a 3 minute cooling time, and a 10 cubic feet per minute (CFM) fan, the furnace block temperature will be 20°C above the ambient temperature after repeated sample analyses. In the first prototype unit, a 50 CFM fan is used where 60% of the air is ducted to the furnace and 40% of the air is ducted to the furnace power supply located underneath the electro-optics plate.

2.5 GRAPHITE FURNACE POWER SUPPLY

The peak current requirement of the PWMA graphite furnace is approximately 500 amperes. This defines the peak capacity requirement of the power supply. The power supply must be lightweight, capable of operating at 115/230 VAC ±10%, 50/60 Hz, and sized for packaging in one container. No off-the-shelf power supply is available that meets all the above requirements; therefore, an entirely new approach was initiated for the Graphite Furnace Power Supply (GFPS) design.

Commercial GFPSs usually weigh from 50 to 100 pounds. The weight is primarily due to the heavy transformer employed since most of the commercial power supplies are operated at 60 Hz. The requirement for magnetic materials is drastically reduced when the transformer is operated at a higher frequency. The PWMA GFPS can be operated at a maximum of 12 kilohertz (kHz). The high current is achieved by using a series resonant power supply that uses silicon controlled rectifiers (SCRs) as the switching elements. Automatic commutation of the SCRs occurs as the resonant current reverses through zero. In operation, current pulses of different frequencies are supplied to the graphite furnace tube. The frequency of the current pulses control the output current, which is sensed by a feedback loop. In this type of high current application, the switching losses have become a limiting factor. Thus, high current asymmetrical SCRs (ASCR), which have an on/off time of approximately ten microseconds, are used in the PWMA furnace power supply. An additional feature of the ASCR is that the waveform is sinusoidal, which minimizes radio frequency interference. The performance of the graphite furnace is discussed in Paragraph 3.5.

2.6 ARGON SUPPLY

Argon gas is used to inhibit oxidation of the external surface of the graphite tube and to remove oil residue and atomic vapor from the inside of the graphite tube. The pressurized argon also holds the furnace blocks so that the graphite tube is in close electrical contact with the two graphite end rings.

The PWMA has a self-contained system of argon gas. The argon gas is stored in a lightweight filament-wound pressure vessel having an internal volume of 2.4 liters, a weight of 3 pounds, and a rated internal pressure of 3000 psig. At

3000 psig, the total gas capacity is 480 standard liters and is enough for about 400 analyses. The vessel is rechargeable. The argon supply system is shown in Figure 6. Gas stored in the pressure vessel flows to a regulator that reduces pressure to 50 psi. The restrictors control the gas flow rate to the internal and external areas of the graphite tube and to the furnace actuator. A second regulator reduces the gas pressure from 50 psi to 4 psi for the sample introduction system.

The internal argon flow in the graphite tube purges atomic vapor during formation and, therefore, affects the sensitivity of wear metal detection. Depending on the wear metals being analyzed, two different internal argon flow rates are used. Flow switching is controlled by solenoid valves. Since the argon flow rate is a function of pressure, the output of the argon pressure regulator must be stable to prevent changes in sensitivity due to variation in argon flow. A compact, single-stage pressure regulator was designed for the PWMA; this regulator can maintain the argon outlet pressure at 50 ±5 psig from an inlet argon supply pressure of 3000 to 70 psig.

2.7 SAMPLE INTRODUCTION SYSTEM

The unique sample introduction system developed for the PWMA emphasized simplicity to minimize operator error. Undiluted oil samples are injected directly, thus eliminating dilution solvents, the dilution step itself, and dilution errors. As shown in Figure 7, the oil sample is drawn to the step or upper end of the sample tip by capillary action. The volume of the sample tip bore, then, constitutes the desired sample volume. The sample is dispensed by an argon gas pulse controlled by two solenoid valves and a gas cylinder housed in the "pistol" handle.

The design and material of the sample introduction tip affects the precision of the sample introduction system. Commercial disposable polypropylene tips were initially tested and the results were not satisfactory. The tapered shape of the commercial tips promoted oil sample splattering inside the graphite tube, and small beads of oil sample adhered to the tip interior. A straight-bore teflon tip was then designed to reduce the sample splattering and to provide a cleaner expulsion. An additional design feature is a shoulder on the PWMA sample introduction tip. The operator places the filled sample tip into the

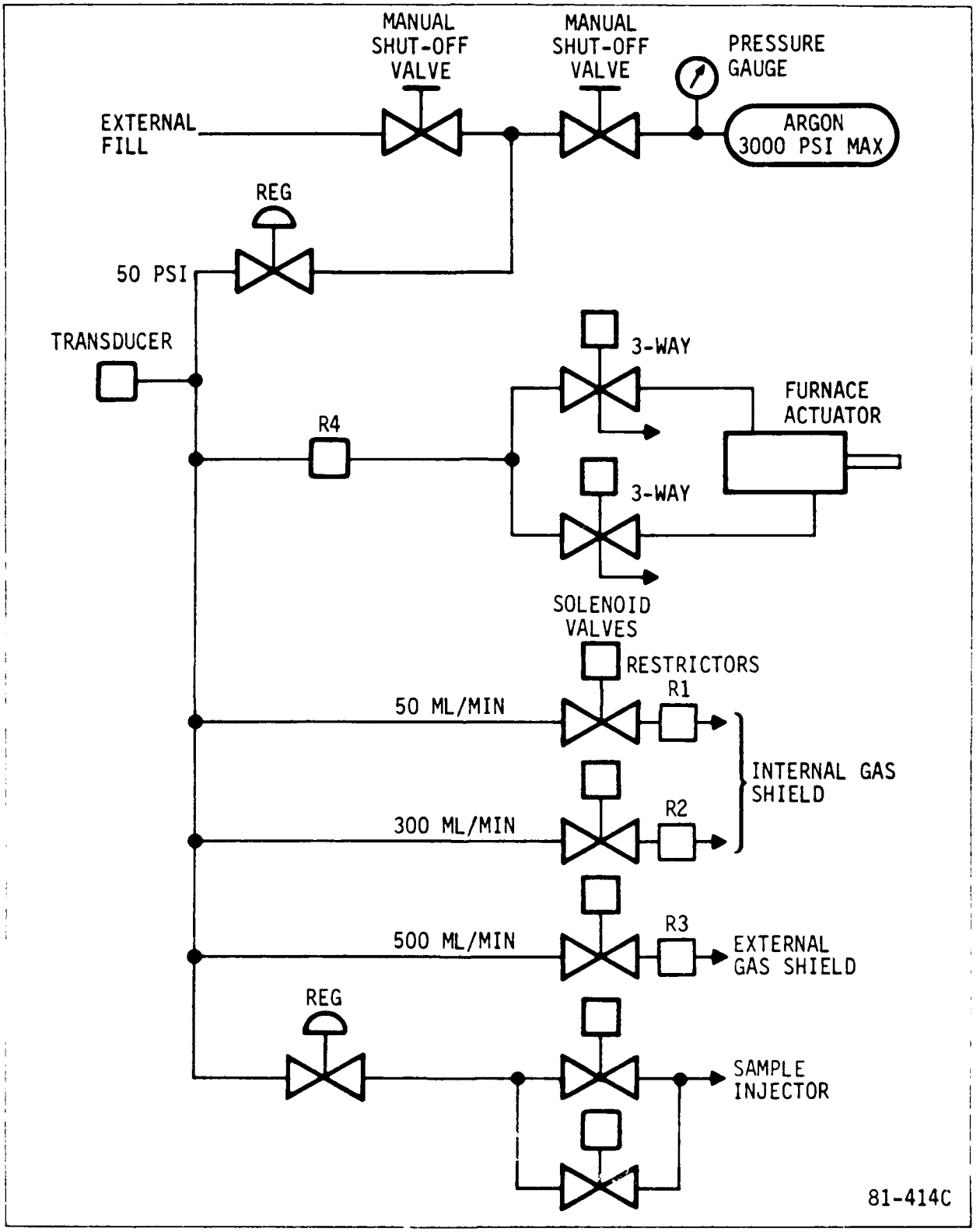

FIGURE 6. PWMA Argon Supply Schematic

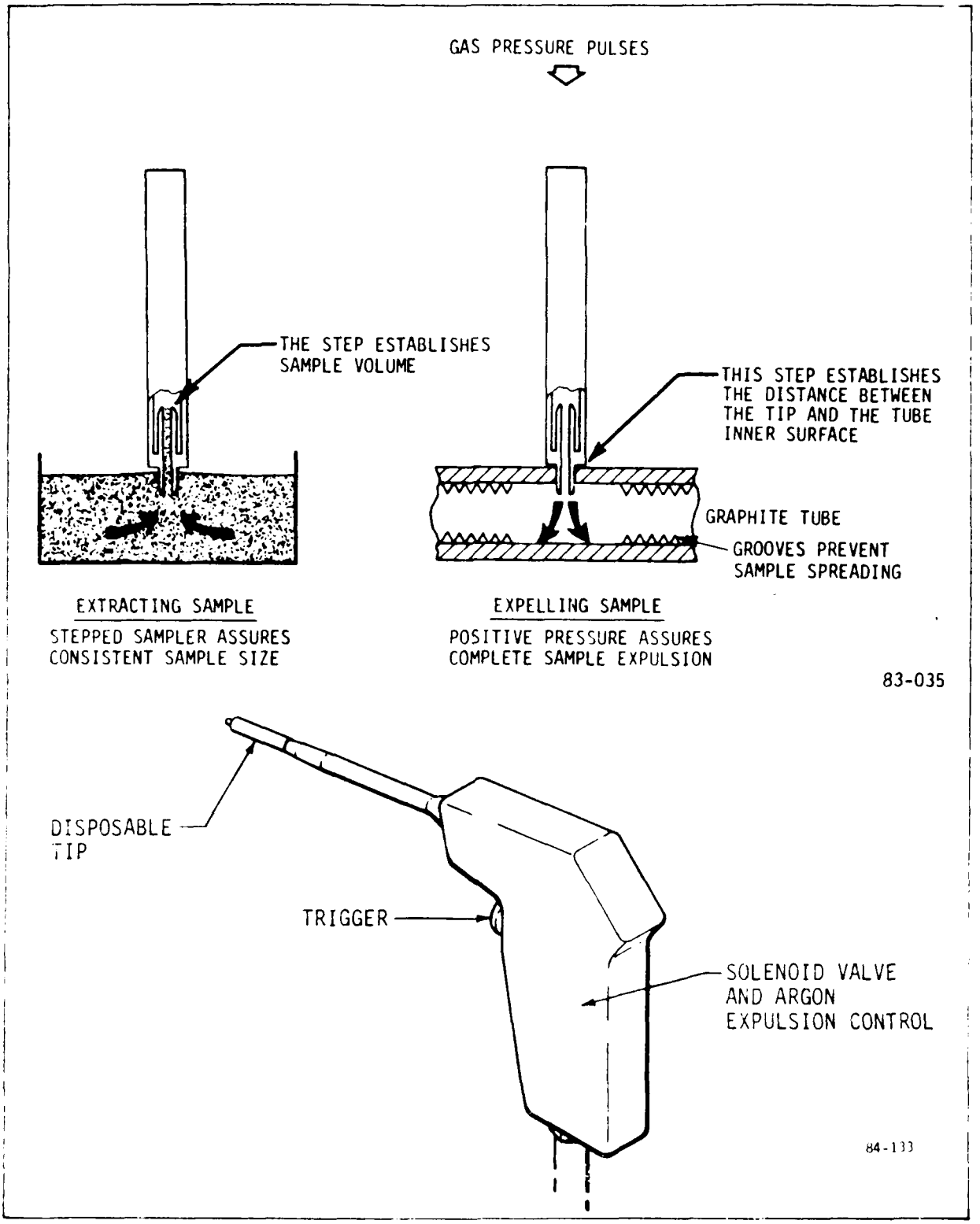

FIGURE 7. PWMA Sample Introduction System

injection port of the graphite tube until the shoulder of the tip rests on the tube itself. This design assures that the tip is always in the same position each time, and ensures that the tip-to-tube distance, selected to minimize splatter, is always the same. The trigger is then depressed, introducing the oil sample into the graphite tube.

2.8 ELECTRONICS

A PWMA system block diagram is illustrated in Figure 8. As shown in the upper left corner, the 115/230 VAC power drives the low voltage power supplies, printer, fans, and graphite furnace power supply. The ±12 VDC and +5 VDC power supplies furnish power for the microcomputer alphanumeric display, electrometers, solenoid valve drivers, and GFPS control board. The +24 VDC power supply provides power for the photomultiplier and HCL power supplies.

The signal processing sequence is illustrated in the center area of Figure 8. Emission lines from the HCLs are focused by transfer optics through the graphite furnace and into the polychromator, where the signals are detected by photomultipliers and are amplified by electrometers. The analog voltage output from the electrometers, representing the light intensities of the received signal, passes through a multiplexer to the analog/digital (A/D) converter. The digitized signals are stored in Random Access Memory (RAM) for absorbance calculation. Finally, the concentrations for the nine wear metals are calculated and printed out as hardcopy or are optionally displayed on the front panel alphanumeric display.

The graphite furnace control loop starts from the input/output (I/O) interface block, as shown at the lower-right corner of Figure 8. The start button initializes the furnace controller, which drives the GFPS according to a predetermined atomization cycle. In parallel, valve drivers for the argon supply are also energized following a programmed sequence. Several protection circuits are incorporated into the graphite furnace assembly and connected to front panel alarm indicators.

The card rack consists of seven circuit boards and an interconnect board. The GFPS controller, HCL current monitors, argon valve drivers, and alarm circuits are distributed among two digital circuit boards. The other five boards consist

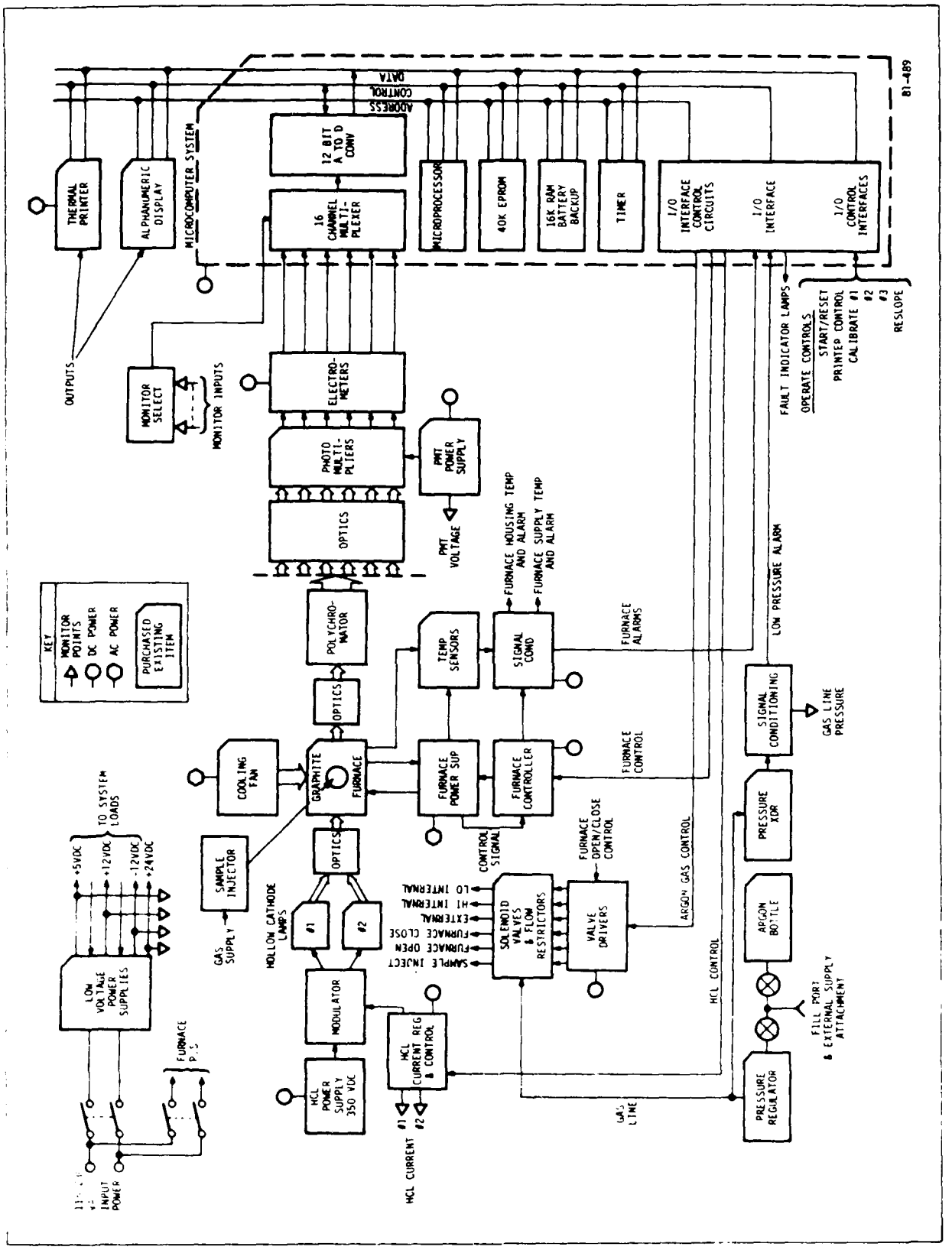

FIGURE 8. PWMA System Block Diagram

of two I/O programmable timer boards, a 16 kbyte RAM board, a 16 channel analog input and A/D board, and a microprocessor (MPU)/40 kbyte Electrically Programmable Read Only Memory (EPROM)/serial interface port (RS232) microcomputer board. Wires extending from the interconnect board are terminated in connectors for ease of service.

All optics assemblies, i.e., source-transfer optics, HCLs, and the polychromator, are positioned on an optics baseplate. The PMT power supply and electrometers are mounted on the baseplate adjacent to the polychromator to minimize noise pickup. The HCL power supply and modulator are located adjacent to the HCLs to minimize the length of leads and modulation interferences. The GFPS is coupled directly to the graphite furnace, which improves efficiency by reducing line losses.

2.9 SYSTEM OPERATION AND SOFTWARE

2.9.1 CONTROL PANEL FUNCTION

The control panel and the sub-panel are illustrated in Figures 9a and 9b. The POWER pushbutton switch turns on the PWMA power. When the READY light is illuminated, the operator may introduce a sample and push the START button to initiate the analysis cycle. The FURNACE switch under the sub-panel opens and closes the furnace for graphite tube replacement, which is required approximately every 150 analyses.

The concentration of the wear metals, selected with the OUTPUT selector, may be displayed on the alphanumeric display. When the OUTPUT selector is set at the DIAG position, the diagnostic functions, are displayed. The FUNCTION selector allows the operator to set up and calibrate the PWMA to assure proper performance. When a new HCL is installed, the mode selector is placed at the SETUP position to properly align the lamp. TUBE COND initializes a temperature program to condition a new graphite tube.

For routine operation, the operator sets the FUNCTION switch to the AUTO ZERO position and injects a blank oil sample; he then introduces three calibration standards, using CAL I, CAL II, and CAL III positions, respectively. The PWMA now is ready for analyzing unknowns with the FUNCTION switch in the ANALYSIS

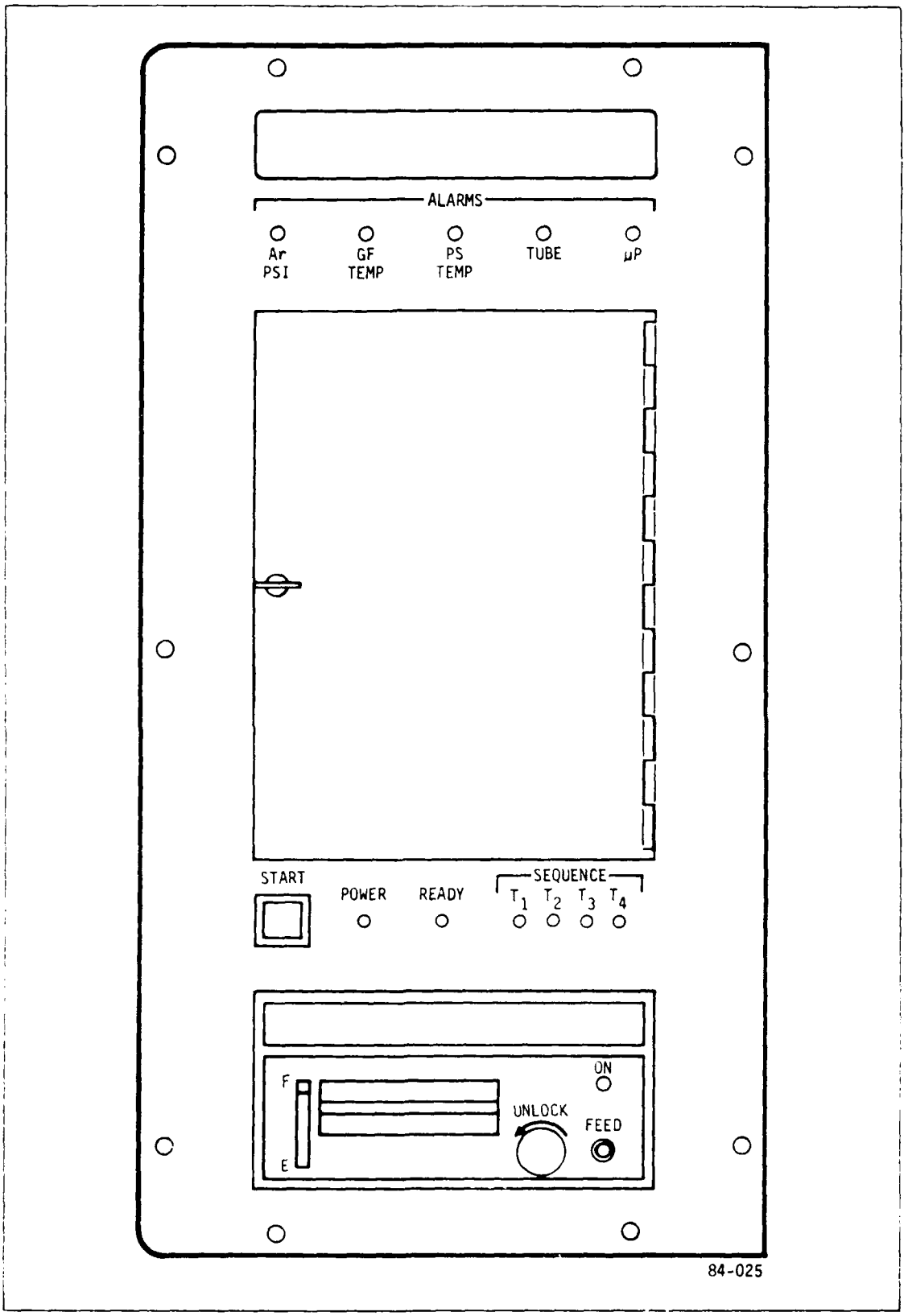

FIGURE 9a. PWMA Control Panel

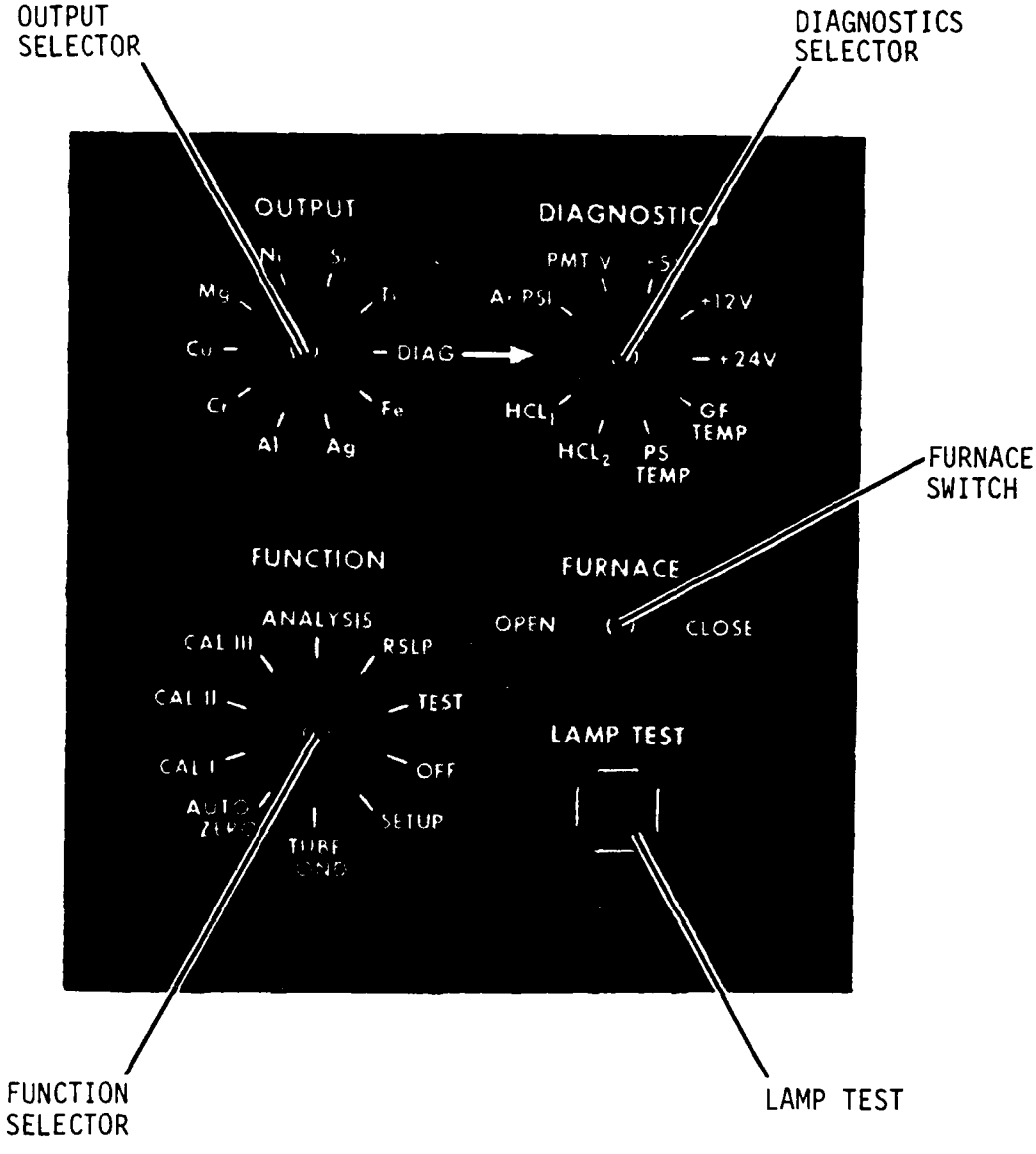

FIGURE 9b. PWMA Sub-Panel

position. The concentration of the unknown samples is measured and calculated according to the calibration curves constructed with the three calibration standards. The RSLP (reslope) function can be used periodically to correct any small sensitivity drift.

Five alarm indicators are provided; the appropriate alarm light illuminates for the following conditions: the argon pressure is incorrect; the furnace block or the GFPS is overheated; the graphite tube is cracked; or the microcomputer has a malfunction. The LAMP TEST button is used to ensure that the lamps are functional. An audible alarm also alerts the operator for each of these alarm conditions.

2.9.2 SOFTWARE ORGANIZATION

The PWMA software is written primarily in PASCAL. The entire program is subdivided into modules and linked together. The module chart is shown in Figure 10. The microcomputer initializes itself when the power is turned on. After the READY light illuminates and the START button is pushed, the microcomputer scans the FUNCTION selector and branches to the selected operating module. As an example, in the ANALYSIS mode, the microcomputer first initiates the preatomization and atomization cycle according to the parameters in the data acquisition table and the furnace table. The graphite furnace then accomplishes a predetermined standard cycle, the data collected are analyzed, and the tolerance of the data is checked to ensure the proper usage of the calibration routine. Parameters such as furnace temperature, ramping time, argon flow rate, and data acquisition time are stored in EPROMs. This type of storage allows the parameters to be changed during the development stage. With this modular programming approach, each module can be individually coded and tested. The microcomputer has a capability to communicate with external devices via an RS232 port. However, the communication software is not written in for the prototypes.

2.10 SYSTEM PACKAGE

2.10.1 FURNACE-OPTICS CONTAINER

The PWMA is packaged into two containers; the furnace-optics container and the electronics-argon container. The furnace-optics container, illustrated in

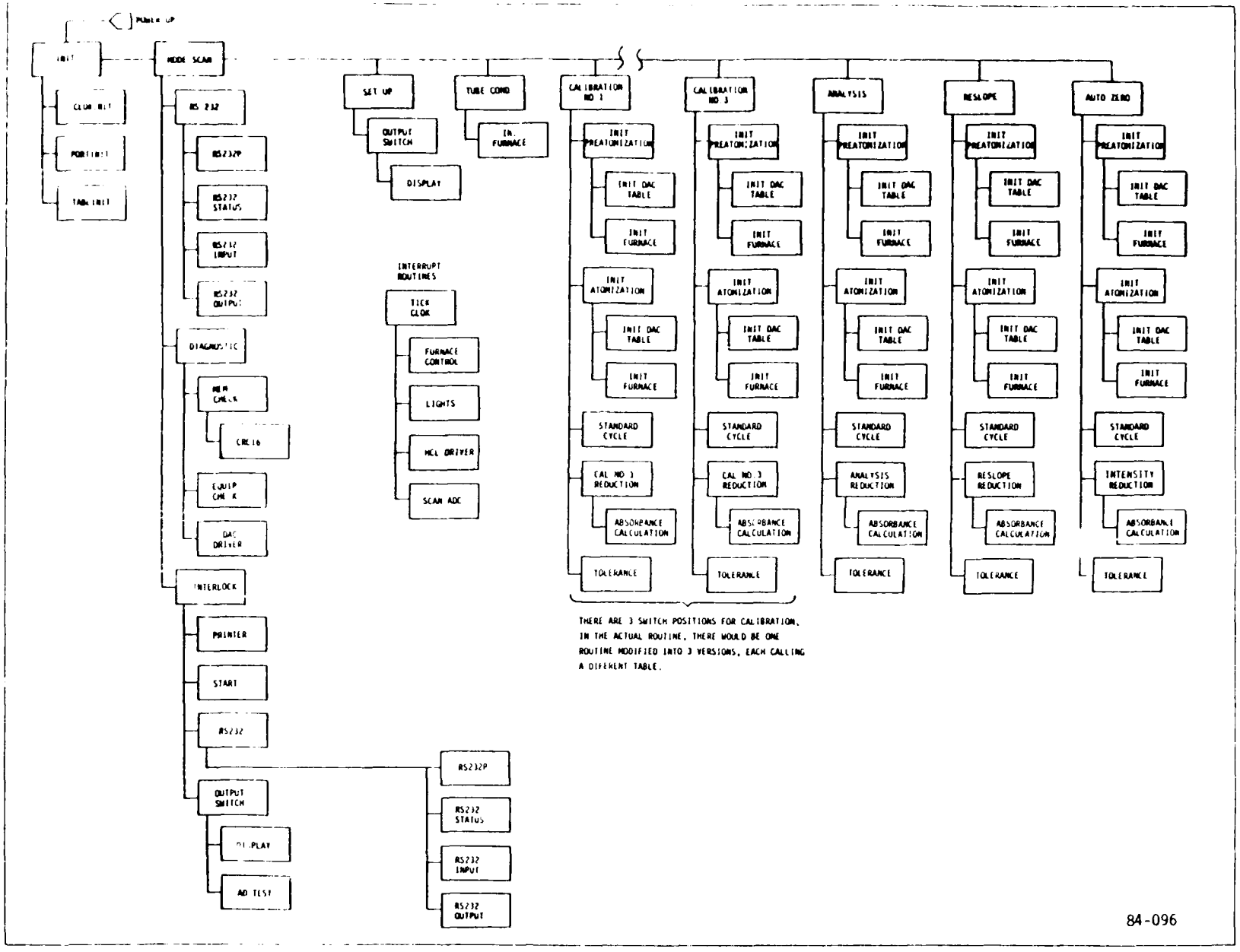

FIGURE 10. PWMA Software Module Chart

Figure 11, weighs 60 pounds. The graphite furnace is mounted in the front of the container and is aligned with the optical path. The GFPS is mounted underneath the electro-optics plate. Argon gas for the graphite furnace is provided by a pneumatic interface located on the right side of the container. Solenoid valves, flow restrictors, and plumbing for the argon gas are also mounted in the container. The optics subassemblies (HCL, transfer optics, polychromator, etc.) are mounted on a honeycomb mounting base chosen for light weight as well as for optical stability. The optics mounting base is shock-mounted within the container for additional protection and stability. The furnace-optics container is fitted with a sealed enclosure to provide light-tight protection for the polychromator, as well as to provide dust and humidity protection for the entire assembly.

2.10.2 ELECTRONICS-ARGON CONTAINER

The electronics-argon container, illustrated in Figure 12, weighs about 40 pounds. The card cage is mounted in the lower right side and is accessed via the top cover. The argon supply tank, a lightweight filament-wound pressure vessel, is mounted at the rear of the container. The argon pressure regulator, fill-shutoff valving, and pressure gauge are mounted on a common manifold connected to the supply tank. The PWMA control panel, located on the left side of the cover plate, includes the controls, display, and a thermal printer. Interface cables (electronics and argon pneumatic line) are stored under the container cover.

2.11 ENVIRONMENTAL CONSIDERATIONS

2.11.1 TEMPERATURE

The operating temperature range of the PWMA is -18°C to 57°C and the storage temperature range is -55°C to 70°C. Considering an ambient temperature of 20°C, the total operating temperature excursion is then ±37°C. This temperature span affects the performance of optics, PMTs, and electronic components.

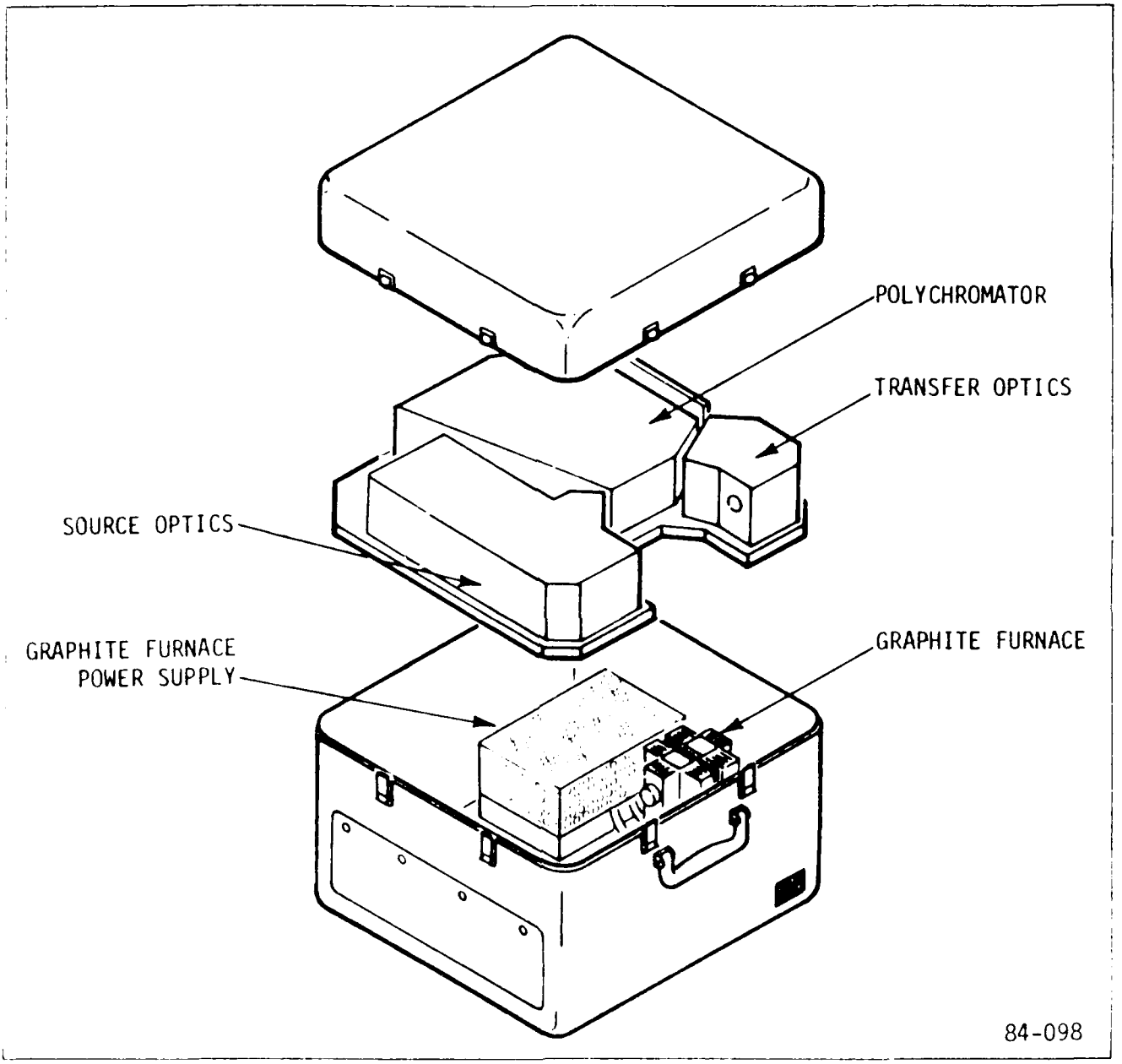

FIGURE 11. Furnace-Optics Container

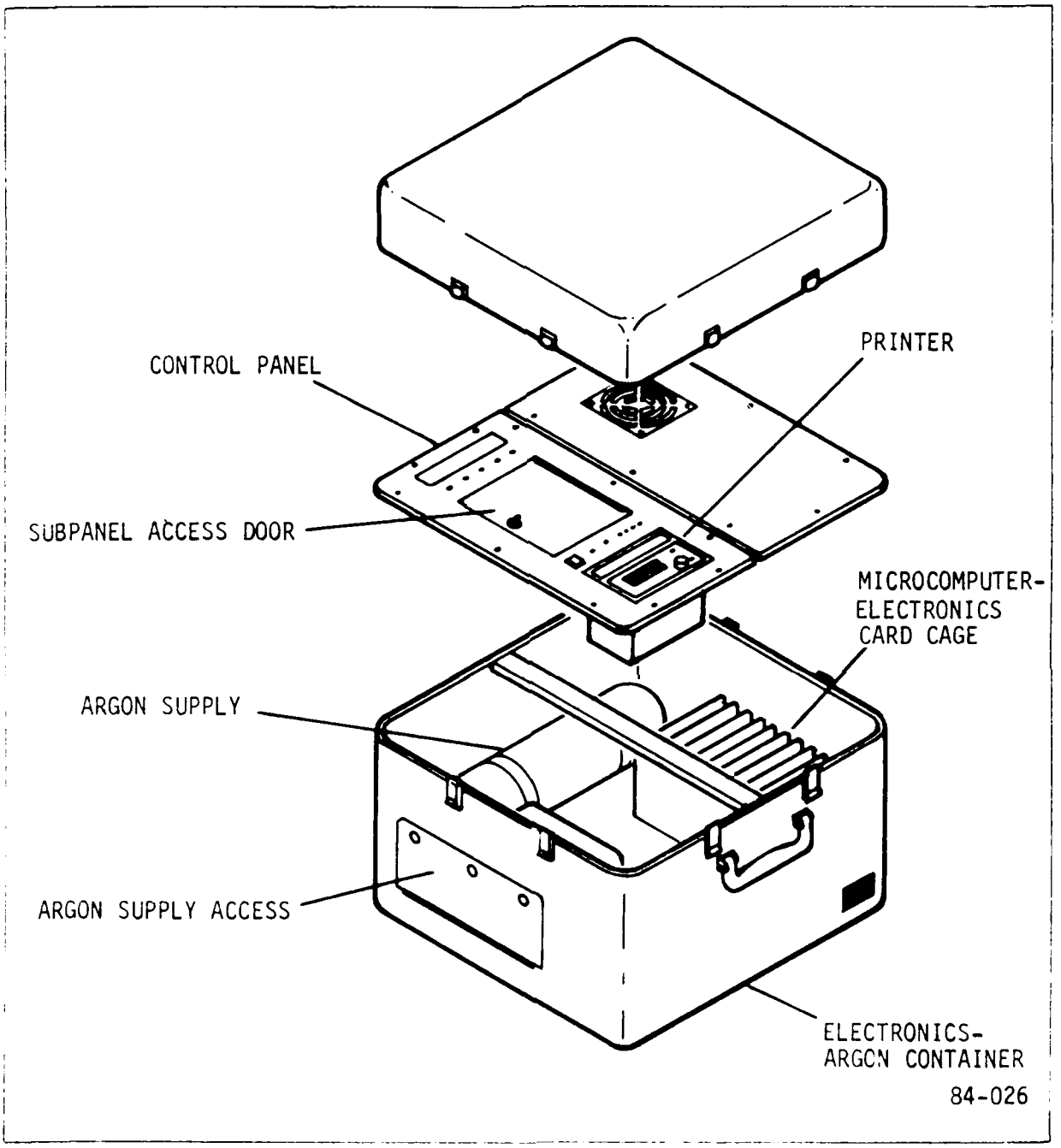

FIGURE 12. Electronics-Argon Container

The polychromator is the most critical assembly in terms of temperature stability. With an increase in temperature, the grating material used in the polychromator will expand and the groove spacing will increase. According to the grating equation (Paragraph 2.2.2), the diffraction angle will then decrease and the focal point will displace from the exit slit. Fused quartz, which has a thermal coefficient of expansion of 0.5×10^{-6}/°C, was selected for the grating blank. The maximum change in the groove spacing at ±37°C will produce a maximum wavelength error of ±0.008 nm at the chromium 428.9 nm line, and the errors decrease at shorter wavelengths. By using the quartz blank, the grating expansion effect becomes insignificant with respect to the resolution requirement of the PWMA. Another important consideration is the structural material of the polychromator frame. As the frame expands, the entrance slit moves away from the grating and the object distance becomes longer. The image distance then becomes shorter and the image is focused in front of the exit slit, resulting in a defocusing effect. To minimize this effect, low expansion Invar alloy with a thermal expansion coefficient of 1.62×10^{-6}/°C was employed as the structural material. Given the geometry of the PWMA polychromator, the maximum increase in image width at the exit slit for the design temperature range of ±37°C is less than 0.001 nm, which again is insignificant. However, if stainless steel, with a thermal expansion of 17.3×10^{-6}/°C, were used, the degraded performance would not be negligible.

The performance of the PMTs also varies with temperature. The PMTs selected for the PWMA have a cesium-antimony cathode. Cesium is a relatively volatile material that starts to evaporate at temperatures within the designed operating temperature range. Information obtained from the PMT manufacturer shows that the mean time between failures (MTBF) at 25°C is 50,000 hours and at 60°C is 5000 hours. Sensitivity of the PMT also changes with temperature. At 57°C, the anode sensitivity is approximately 25% lower than the sensitivity at 25°C and the dark current increases rapidly at that higher temperature. Fortunately, in the AA measurement, the absorption signal is the ratio of the light intensities; thus, slow variations in photomultiplier tube sensitivity do not significantly affect the result.

The temperature characteristics of electronic components were also considered. In general, the leakage current, which affects the performance of a semiconductor device, becomes excessive at temperature extremes. EPROM chips are more

susceptible to elevated temperatures since the leakage current may directly affect the static charge on the memory chip. However, the electronic component selection must also be based on the cost effectiveness.

2.11.2 HUMIDITY

The PWMA is required to operate between 0 to 100% relative humidity. The polychromator is the critical assembly, which is susceptible to humidity effects. The polychromator cover is sealed to the optics baseplate to provide an environmental enclosure. A desiccant cartridge is placed inside the cover to remove any moisture. Replacement of the cartridge is required more frequently in high humidity environments. Electronic components and circuit boards are protected from humidity by conformal coating; in addition, electronic components and circuit boards protection is provided by the military-type containers.

2.11.3 ELEVATION

The operating elevation requirement for the PWMA is from -250 to 15,000 feet. The storage elevation requirement is from -250 to 25,000 feet. The major effect of the elevation change is that the pressure decreases as the altitude increases. At 15,000 feet, the atmospheric pressure is approximately 8 psi. This pressure is still high enough to prevent corona discharge from occurring. Therefore, no special efforts were made to insulate electronic components. A breathing valve is installed on the polychromator cover to equalize the pressure on both sides of the polychromator cover during elevation changes.

2.11.4 INCLINATION

The PWMA will operate at a 15° inclination and may be transported in any position. To meet this requirement, all components in the PWMA are rigidly mounted and can be tilted in any direction. During operation, a tilt of no more than 15° parallel to the axis of the graphite tube axis is recommended, to avoid sample flowing to one end of the tube.

2.11.5 SHOCK

The shock requirement for the PWMA is 30g in mutually perpendicular axes. All optical components are rigidly mounted on an aluminum honeycomb baseplate. The baseplate is shock-mounted to the container structure to protect the sensitive optical components from shock during transportation.

During operation, the baseplate is locked into a fixed position so that proper alignment with respect to the graphite furnace can be maintained. The remaining components are rigidly mounted to the container, without shock absorbers. The two aluminum containers are designed to improve structural integrity.

CHAPTER III

FIRST PROTOTYPE PERFORMANCE

3.1 DATA HANDLING

The PWMA is under complete microcomputer control. Two HCLs containing nine elements are pulsed alternately to provide the absorption lines for the analysis. In the PWMA, HCL No. 1 emits spectral lines for Ag, Al, Cu, Cr, Fe, and Mg and HCL No. 2 emits spectral lines for Ni, Si, and Ti. One feature incorporated into the PWMA is the background correction capability. In AA spectroscopy, the "background" is primarily due to the matrix molecular absorption and scattering. Absorption/scattering usually affects wide band signals instead of the narrow line absorptions that occur in atomic transition. This background contribution can be removed using a correction scheme. Because the multi-element HCLs emit a complex spectrum, there are some emission lines in HCL No. 2, adjacent to the absorption lines of HCL No. 1, which are nonatomic lines. These nonatomic lines serve as background correction lines for the elements in HCL No. 1, and vice versa. As an example, HCL No. 1 emits radiation at 385.99 nm, which is the Fe absorption line. HCL No. 2 emits radiation at 385.81 nm, which is a nonatomic line and will not contribute to the Fe absorption. However, both 385.99 nm and 385.81 nm lines absorb backgrounds that can be measured. Thus, the background signal can be removed by properly processing these two signals.

The PWMA HCL pulsing cycle is shown in Figure 13. Six different intensity signals are measured and the absorbance is calculated according to:

$$A = \log \frac{I_{OS} - I_{DC}}{I_{FS} - I_{FE}} - \log \frac{I_{OB} - I_{DC}}{I_{FB} - I_{FE}}$$

I_{OS} = initial signal line intensity transmitted without absorption
I_{OB} = initial background line intensity transmitted without absorption
I_{FS} = signal line intensity after absorption
I_{FB} = background line intensity after absorption
I_{DC} = dark current of the detector
I_{FE} = furnace emission intensity

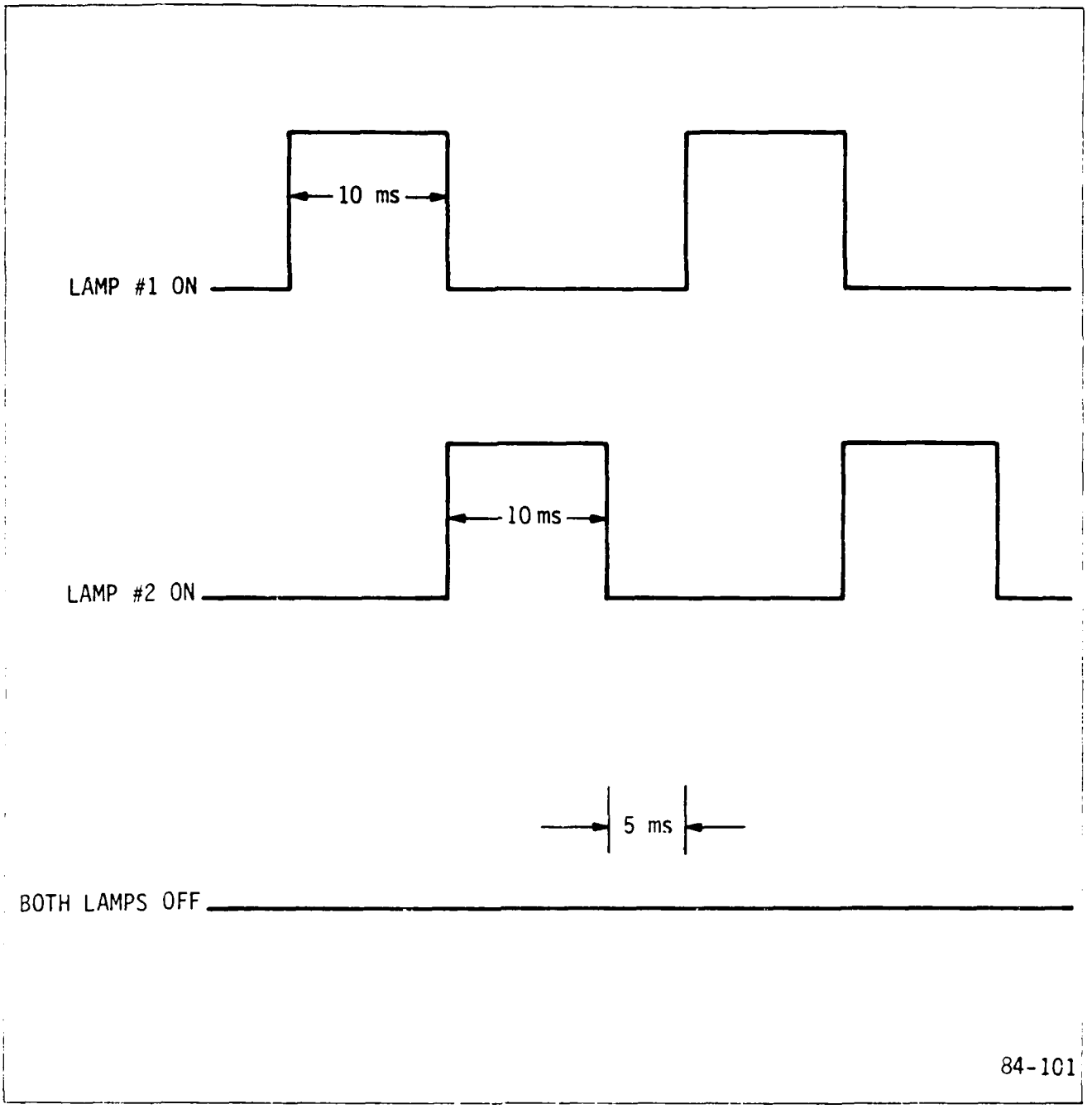

FIGURE 13. PWMA Lamp Pulsing Cycle

The first term represents the atomic absorption signal of interest and the second term represents the background absorption. However, during the testing period, no background signals were found. This was due to the use of a high char temperature, which completely burned out the oil matrix. For simplicity, the background correction was not used, which was done by dropping the second term in the absorbance equation.

The absorbance calculated from the above formula represents a single data point on the absorption curve. For the PWMA application, peak area measurement was selected, primarily because the area measurement was less affected by the furnace temperature variation. The testing data obtained from the commercial instrument also showed that peak area measurements were more reproducible than peak height measurements. The area calculation is simply the summation of each data point over a predetermined sampling time. The number of data points sampled and the period of sampling for each metal are determined from the absorption vs. time curves.

3.2 BRASSBOARD

Prior to the building of the first prototype unit, a brassboard was configured and tested to prove the concept[3]. In the brassboard, optical components were mounted on a laboratory optical table. The polychromator was the same as the final design and was optically aligned with the other components. The transfer optics, including HCLs, toroidal mirrors, beam combiner, and folding mirror were placed at the same positions as the final design with commercial optical mounts which provided three-dimensional adjustment for optimization of focus and alignment. The optical components were enclosed in two separate covers for protection from particulates.

The air/water-cooled graphite furnace was aligned in the optical path. A cooling fan was mounted beneath the furnace and the whole assembly was attached to the optical table. The GFPS was mounted in front of the furnace and shielded by a perforated screen cover. A laboratory argon cylinder was connected to the PWMA regulator. The regulator, solenoid valves, and restrictors were mounted on a board and connected to the furnace with tygon tubings. Laboratory power supplies were used to provide ±12 V dc and +5 V dc power. The HCL power supply and modulator, the PMT power supply, and electrometers were mounted adjacent to

the HCLs and the polychromator, respectively. A Motorola Exorciser was used in the brassboard and all the data were handled by the Exorciser.

The brassboard was tested in August, 1983. After the test, the brassboard was disassembled and most of the subassemblies and components are now being used in the first prototype unit. The performance of the brassboard is described in the interim report.

3.3 FIRST PROTOTYPE CONFIGURATION

The first prototype was configured the same as that shown in Figures 11 and 12. The prototype unit was assembled and tested via a Motorola Exorciser with a floppy disk. After all the functions were verified, the program on the floppy disk was then "burned" into EPROMs. The EPROMs were then installed into the first prototype for its stand-alone operation.

3.4 OPTICAL PERFORMANCE

Throughput and resolution are the two most important performance parameters in the optical assembly. The polychromator was assembled first and the entrance slit was aligned. A microscope mounted on a translational stage was employed to measure the width of the chromium line (428.9 nm) at the focal point. The resolution determined by this method was approximately 0.1 nm, which was close to the theoretically calculated value of 0.08 nm, neglecting geometrical aberations. The chromium line at 428.9 nm was used for focusing and to check resolution, because it is visible to the eye whereas other spectral lines are in the ultraviolet region.

The transfer optics were aligned with the aid of a helium-neon (He-Ne) laser. The emission lines were focused onto the entrance slit of the polychromator. The detection levels and the noise levels for all the wear metal channels were measured. The magnesium channel had the greatest noise, since a weak emission line was selected for magnesium detection. The peak-to-peak noise measured was approximately 15 percent of the signal level, which was consistent with the theoretical shot noise calculation. This noise level was relatively high;

however, integrated peak areas were used for the absorbance calculation, and the noise contribution was reduced by a factor proportional to the square root of the total number of sampling points.

The magnetic field induced by the graphite furnace could affect the PMT response. A magnetic flux probe, which is sensitive to high frequency field, was employed to measure the magnetic field around the graphite furnace during operation. The highest magnetic flux found was at the middle of the two junctions connecting the furnace and the power supply. The magnetic flux, at the region where PMTs are located, was less than 1 gauss. In the PWMA, the PMTs were protected with magnetic shields, but the attenuation of the magnetic field by the shielding material was low. The low attenuation factor was mainly caused by the permeability of magnetic material decreasing drastically at the design frequency. However, for the side-on type of PMT selected for the PWMA, this magnetic field would not change the tube sensitivity in any significant amount. No further improvements were made to the magnetic shield.

3.5 GRAPHITE FURNACE PERFORMANCE

The temperature calibration of the graphite tube was accomplished by three separate procedures, because no single device can measure the entire temperature range. A Chromed-Alumel thermocouple was employed to measure temperatures up to 900°C. The thermocouple was carefully positioned inside the graphite tube. Between 900°C and 1500°C, temperatures were calibrated by a hand-held pyrometer (Pyrometer Instrument, Model 95). The meter was focused at the aperture of the graphite tube. A two-color pyrometer (Ircon 35C10) was used to measure the temperature above 1500°C. A calibration curve of the tube temperature versus the current flowing through the tube was constructed based on these temperature measurements. The accuracy of this calibration curve depends on the accuracy of the three calibration instruments and the experimental conditions. However, the absolute accuracy of the temperature calibration is not critical because the temperature setting for the atomization cycle is empirically determined. The highest temperature of the graphite tube achieved by the furnace power supply is approximately 2900°C depending on the tube used. The effect of the temperature on the analytical performance is discussed in a later section.

Air-cooling of the graphite furnace was tested successfully and was used as the primary testing mode during the brassboard and prototype testing. A thermocouple was attached to the furnace block to monitor the temperature. The peak block temperature of 100°C occurred about five seconds after the end of the atomization cycle; then cooled to 40°C after another three minutes. It was found experimentally that when the cooling fan was operating, it interfered with the external argon flow. As a result, the exterior of the graphite tube was oxidized, which affected the tube life. This problem was resolved by carefully shielding all the leakage path leading toward the furnace. The water cooling capability is still preserved. Preliminary tests showed that water/air cooling modes are interchangeable; however, analytical performance testing using the water-cooling mode should be considered if water cooling is to be used.

3.6 SAMPLE INTRODUCTION SYSTEM PERFORMANCE

The sample introduction assembly of the PWMA allows the introduction of an oil sample into the graphite furnace without dilution. The oil sample is drawn into the sample tip by capillary action and dispensed into the graphite tube by pressurized argon flow. The tip material, configuration, and argon pressure are the parameters that affect performance. After testing with different materials and configurations, Halar (a material similar to Teflon) was selected as the tip material. Argon pressure was optimized for best analytical repeatability. With a higher pressure, the repeatability that was measured gravimetrically improved as a result of "clean expulsion." However, the oil sample splattered inside the tube and caused nonreproducible atomization data. An optimum operating pressure of 4 psi was selected for the design verification testing. The tips are injection molded and the performance is quite satisfactory.

The sampling performances required by specifications MIL-L-7808 and MIL-L-6082 oil are also different. The MIL-L-6082 oil has a viscosity of about 230 centistokes at 37°C. This "thick" oil tends to cling to the sample tip wall and requires a higher pressure for expulsion. The MIL-L-7808 jet engine oil has a typical viscosity of 13 centistokes at 37°C and requires a reduced expelling pressure. To optimize the pressure for either type of oil sample would cause a degraded performance for the other. The best method is to use the same type of oil for both calibration standards and test samples. Therefore, for the design verification test, MIL-L-7808 oil was used for the calibration standards.

3.7 SYSTEM PERFORMANCE

3.7.1 ATOMIZATION CYCLE

The basic graphite furnace AA process involves three basic steps. The furnace temperature is first brought to 100°C to remove water from the sample. The furnace temperature is then raised to an intermediate temperature to ash the sample matrix, e.g. oil. Finally, a very high temperature is reached to atomize the sample. As a general rule, the dry and char temperatures should be ramped slowly to avoid sample bumping. The atomization temperature should be stepped as fast as possible to obtain maximum efficiency and to minimize any chemical interaction within the sample or between the sample and the graphite tube wall. The char temperature is usually set as high as possible to completely ash the sample matrix without losing the elements to be measured. Instrument manufacturers usually publish "cookbooks", which list the standard instrument measurement conditions for each element. The analyst can then use the cookbook as a guide to procedure development. However, the standard conditions listed are for single element analysis.

The atomization cycle for the PWMA must accommodate the atomization conditions for all nine elements, thus requiring a new development approach. Graphite furnace AA is a very sensitive measuring instrument and the sensitivities are too high for most of the elements on the PWMA list. Secondary lines with reduced sensitivities are used for these elements. As an example, the primary line for Fe at 248.33 nm is too sensitive. Selection of the secondary line at 385.99 nm reduces the sensitivity by a factor of 15, resulting in a relatively linear absorption response for sample concentrations from 1 ppm to 100 ppm. The secondary lines originate from the non-ground state transitions in the HCL, i.e., photons emitted by atom transitions from excited state to excited state. Because most of the atoms formed in the graphite furnace are in the ground state and fewer atoms are in the excited states, the absorption sensitivities for these secondary lines are lower. The absorption lines selected for the PWMA are listed in Table 1. The physical locations of the lines on the focal plane must also be considered. For example, Ti is an insensitive element, and the primary line should be used. However, the primary line at 365.3 nm is difficult to

accommodate in the present polychromator design. The absorption line at 398.98 nm was selected at the expense of reduced sensitivity. Furthermore, not all elements have adequate secondary lines. For example, silver has only two absorption lines and both have very high sensitivities. Accordingly, a different method of sensitivity reduction was required, and the method is discussed in the next paragraph.

Table 1. Analytical Lines for the PWMA Brassboard

Element	Wavelength (nm)	Sensitivity Reduction*
Ag	328.07	1
Al	256.80	12
Cr	428.97	5
Cu	218.17	11
Fe	385.99	15
Mg	202.58	30
Ni	341.47	4
Si	251.61	1
Ti	398.97	2

*Estimated from Flame AA data published by AA Manufacturers

A commercial instrument, the Perkin-Elmer Model 5000, was employed for developing the PWMA atomization cycle. All wear metals on the design list were tested individually and their atomization conditions were characterized. An atomization cycle that accommodates all the conditions was developed and tested. The atomization cycle used for the first prototype is described below:

A. Ramp the temperature from ambient to 100°C in 5 seconds and hold for 5 seconds.

B. Ramp the temperature from 100°C to 800°C in 10 seconds and hold for 10 seconds.

C. Ramp the temperature from 800°C to 1300°C in 8 seconds and hold for 2 seconds.

D. Step the temperature from 1300°C to 1900°C in 2 seconds and hold for 2.5 seconds.

E. Step the temperature from 1900°C to 2200°C in 1 second and hold for 1.5 seconds.

F. Step the temperature from 2200°C to 2700°C in 0 second and hold for 2.5 seconds.

G. Step the temperature to 2800°C and hold for 2.5 seconds.

Step A removes water from the oil sample. Traces of water may originate from the oil or from contamination of the sample during rainy weather. The temperature is then raised to 800°C to completely ash the oil matrix. Silver is analyzed in the temperature ramp from 800°C to 1300°C. As discussed in the preceding paragraph, silver is a very sensitive element and no adequate secondary line is available. Analyzing silver on this long temperature ramp tends to atomize it slowly, thus resulting in a broad peak without saturating the absorbance signal. Although analyzing an element on a ramp is not recommended, the peak area measurement of silver has been proven to be repeatable. After the silver analysis, the temperature is stepped to 1900°C and then to 2200°C where copper, magnesium, iron, nickel, and chromium are measured. The optimum atomization temperatures for the above five metals are somewhat different. The temperatures were so chosen to slow the atomization to minimize the saturation effect and also to avoid the loss of Si. Finally, the temperature is quickly stepped to 2700°C, where silicon, aluminum, and titanium are atomized. The quick temperature stepping is achieved by overshooting the current of the graphite furnace power supply. Using this maximum power burn, fast temperature increase is accomplished and maximum atomization efficiency is achieved.

The internal argon gas flow rate is another parameter that affects performance and sensitivity of analyses. From Step A through Step D, argon flow rate is maintained at 300 ml/min to effectively purge the smoke created by the oil matrix and to reduce the sensitivities for the six sensitive elements. At Step E, the argon flow is stopped to promote the sensitivities of the remaining three less sensitive elements. At the end, the high flow rate is resumed to purge the residues.

3.7.2 ANALYTICAL PERFORMANCE

Multi-element samples were diluted from individual CONOSTAN standards prepared in hydrocarbon oil at 5000 ppm concentration. Since each wear metal has a required concentration range, the sample concentrations are expressed as a percent of the full scale. A 100% full scale standard contains 100 ppm iron, 50 ppm magnesium and aluminum, 40 ppm copper, 30 ppm nickel, 20 ppm silicon and titanium, and 10 ppm silver and chromium. Different samples were prepared in MIL-L-6082 grade 1100 reciprocating engine oil, MIL-L-7808 oil, and MIL-L-23699 oil.

Ideally, the analytical curve of absorbance versus concentration should be linear to obtain maximum accuracy. However, the linear working range for AA is relatively small and, in most cases, the analytical curve tends to bend toward the concentration axis at higher concentrations. In the PWMA, the analysis is further complicated by measuring nine elements in one analysis sequence. Thus, the atomization condition of an element cannot be adjusted individually to shift the work range of that element into a linear region. For example, the analytical curves for magnesium bend heavily toward the concentration axis. This is primarily because magnesium is a very sensitive element and saturation occurs at higher concentrations. Also, silicon is insensitive because part of the silicon is lost during the previous cycle. The causes and possible improvements are discussed in the next section.

CHAPTER IV
ENVIRONMENTAL TESTS

4.1 SHOCK TEST

The shock test was designed to ensure that the PWMA can meet the rough handling requirement. The PWMA was subjected to 30 g, half-sine shock pulse with a pulse width of 11 msec. Figure 14 shows the computer plot of the shock pulse. Three separate shock pulses were applied along three mutually perpendicular axes, a total of nine shocks for each container.

The test was conducted at Abec Environmental Laboratory, Industry, CA. During the tests, a transducer was mounted on the optical plate to sense the actual shock level received by the optical plate. The transducer was connected to a storage oscilloscope as shown in Figure 15. Because the optical plate is shock-mounted to the container, shocks registered by the transducer were less than 5 g. The transducer was then placed on the outside of the container. Approximately 25 g instead of 30 g was seen on all three axes. The discrepancy between the input pulse level and the pulse level received by the container is due to the experimental setup. The container was set on top of the shock table and held with two tie-down straps. The shock pulses were applied horizontally. Thus, the straps could absorb part of the energy of the shock pulse. To conduct an optimum shock test, a fixture is required to secure the unit being tested. The fixture itself should be heavier and structurally stiffer than the test unit so that it will not affect the test unit. The PWMA has no provision for mounting to a fixture, so the best alternative was used.

In order to increase the shock level received by the PWMA, the feet of the container were placed in the mounting holes on the shock table. The shock level registered at the container was greater than 40 g. However, it was felt that it was an uncontrolled experiment and no further test was performed.

Since maintaining the integrity of the optics during the handling is the main concern, electrometer outputs that show the optical signals were measured after shocks on each axis. The signals measured were within tolerance. A post-shock

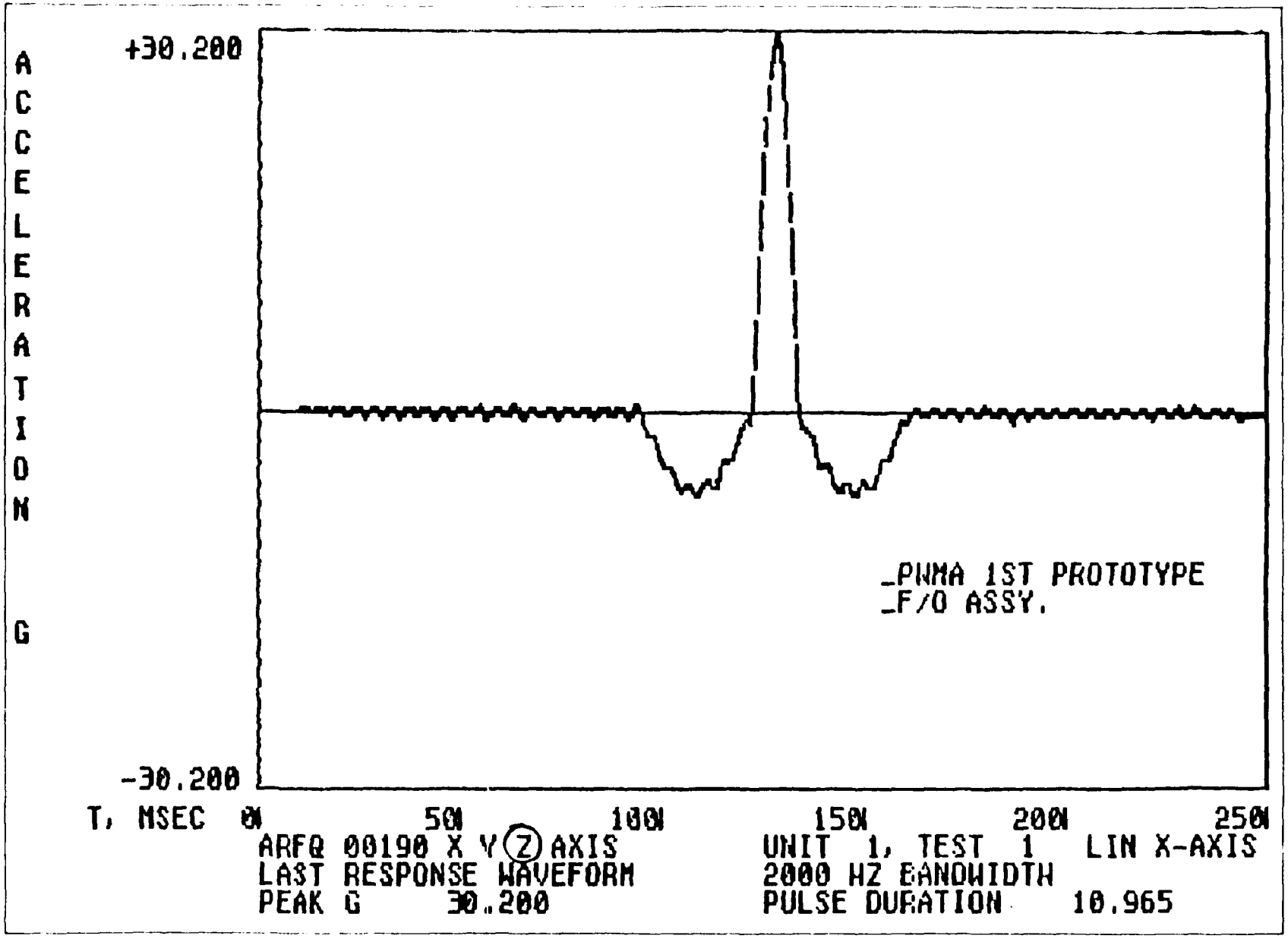

FIGURE 14. Input Pulse for Shock Test

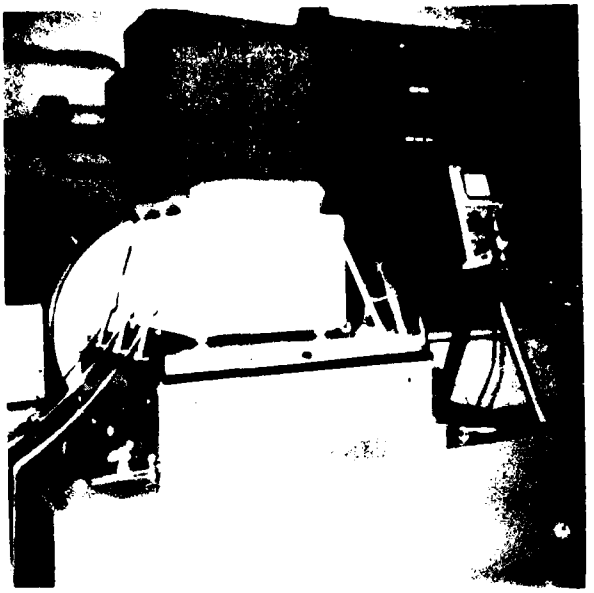

FIGURE 15. Shock Table

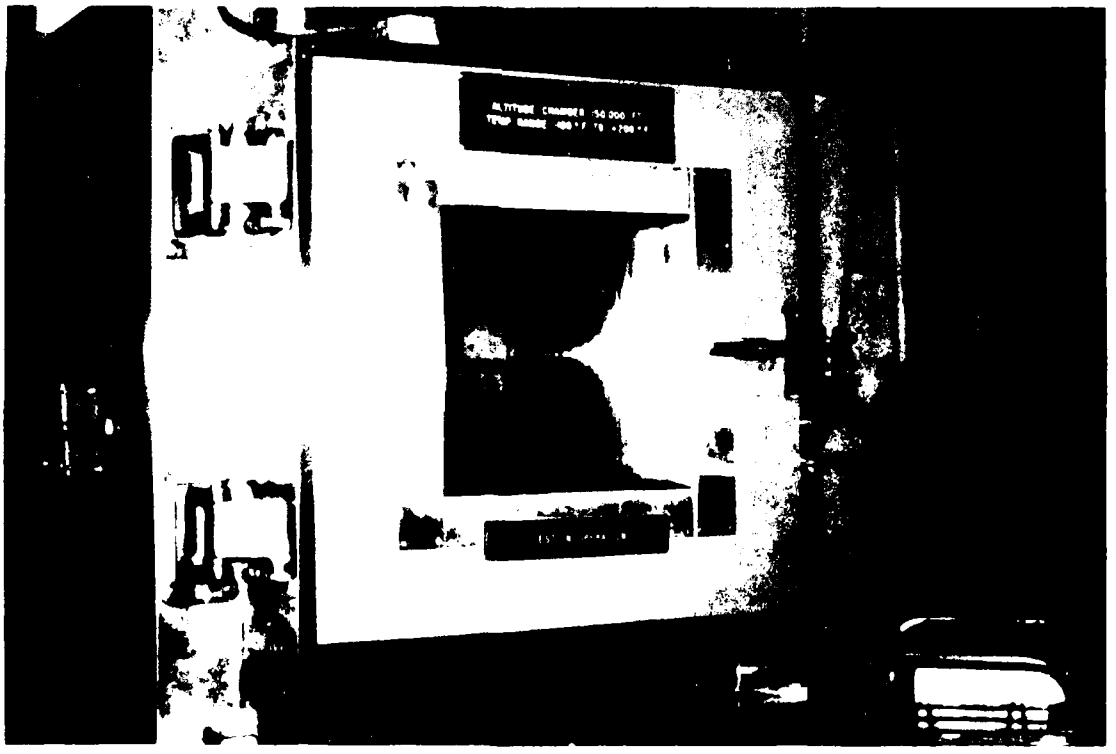

FIGURE 16. Altitude Chamber

performance test was conducted after the PWMA was returned to Perkin-Elmer. The data is attached to Appendix A and no change in performance was shown.

4.2 ALTITUDE TEST

The altitude test was conducted to determine the effects of reduced pressure on the PWMA. High altitude was simulated by pumping down the test chamber and the below sea level altitude was simulated by pressurizing the test chamber. The PWMA was tested in Perkin-Elmer's test chamber, as shown in Figure 16, and was subjected to the following profile:

a. Raise to 25,000 feet (equivalent to 282 mmHg) and settle for 15 minutes.

b. Rapidly drop to 15,000 feet (equivalent to 429 mmHg) and settle for 15 minutes.

c. Change to -250 feet (equivalent to 767 mmHg) and settle for 15 minutes.

d. Return to room ambient.

Due to the vacuum requirement of the altitude chamber, no functional test was performed during the test. The functional test was conducted afterwards and no change in performance was observed.

4.3 TEMPERATURE TEST

The temperature test was conducted to determine the resistance of equipment to both low and elevated temperatures that may be encountered during operation or in storage. The test chamber is shown in Figure 17. A thermocouple was attached to the furnace-optics container to monitor the temperature of the unit.

4.3.1 COLD TEMPERATURE TEST

The PWMA was placed in the temperature chamber and the temperature was first lowered to -55°C. The unit was stabilized for 45 minutes to simulate the

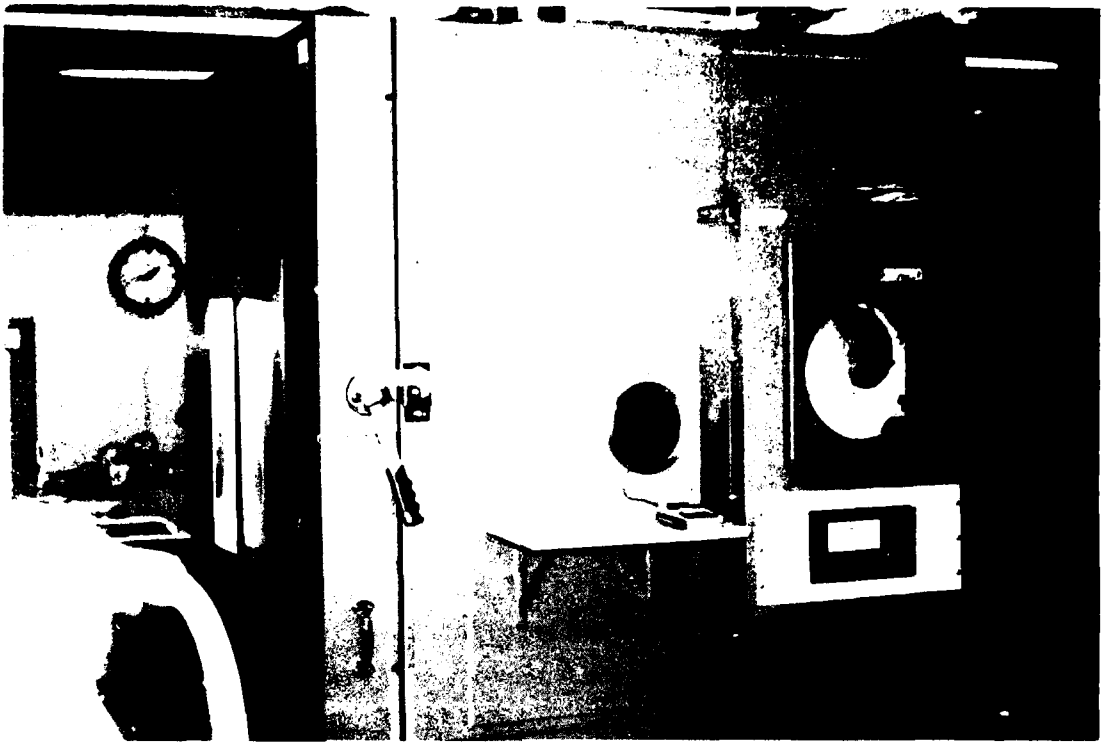

FIGURE 17. Temperature Chamber

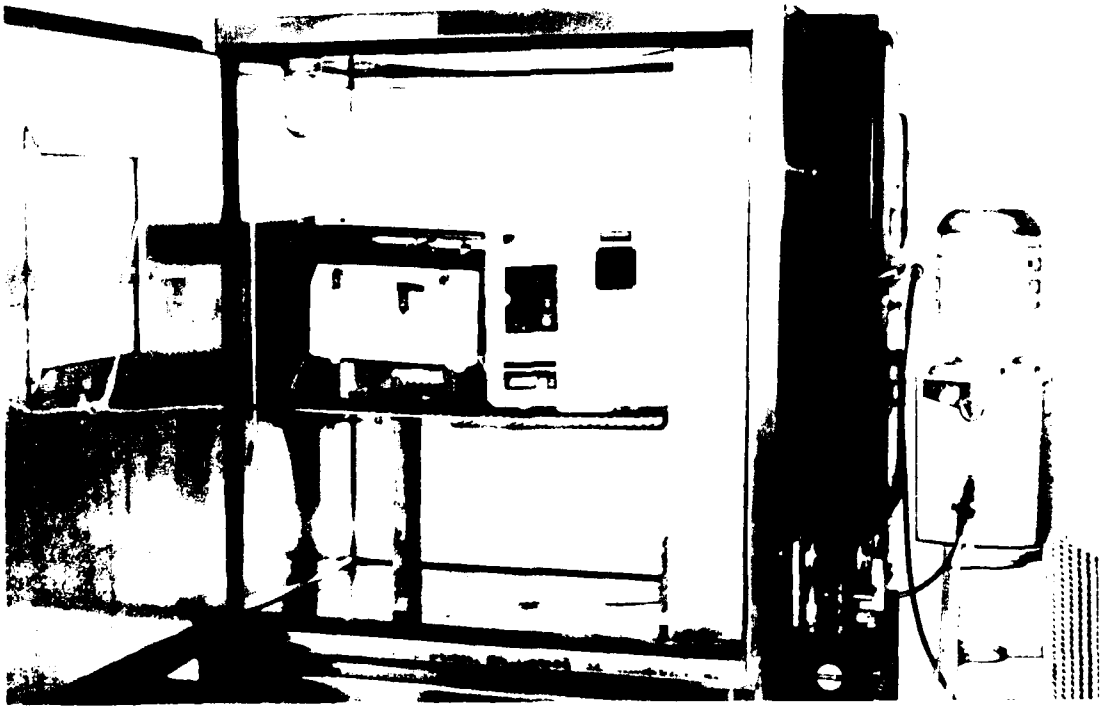

FIGURE 18. Humidity Chamber

storage temperature. The temperature was decreased to -80°C and the unit was stabilized for 1-1/2 hours. Some frost formed at the furnace windows. Since it is impractical to open the temperature chamber to inject an oil sample (this would introduce frosting), three blank burn cycles were executed via a side port on the temperature chamber. The burns indicated that the overall system was functioning. The heat generated by the burns also cleared the frost from the furnace windows. Electrometer outputs were measured after the burns and the signal levels were slightly higher than those measured at room ambient. This indicates the focusing of the optics is not significantly affected by the temperature change as described in Paragraph 2.11. The slightly higher outputs occurred because the PMT gain is higher at low temperature.

Some problems also occurred at the low temperature. The performance of the printer degraded and the printouts were barely recognizable. This is a limitation of the thermal type printer. One of the solenoid valves developed a leak and the Argon bottle was empty after the cold temperature test. A more reliable valve will be used for the next five units. Unfortunately, the new valve only has an operating temperature rating from 0°C to 80°C. Therefore, in a cold environment, the manual valve on the Argon bottle should be closed when the unit is not in use. A caution message in the operating manual will address this requirement.

It is very difficult to make an accurate analysis at temperatures below 0°C. The main difficulty is the operator's inability to repeatedly inject an accurate amount of oil sample.

4.3.2 HIGH TEMPERATURE TEST

For the high temperature test, ten oil samples were processed at 57°C by opening the test chamber. Because of the large thermal capacity of the PWMA, opening the chamber and quickly injecting a sample would not disturb the thermal equilibrium significantly. Test data indicates that the performances are the same as that at the ambient temperature. However, several anomalies occurred and their causes and solutions are discussed below:

a. When raising the temperature from low to high, the argon interconnecting hose ruptured. Presumably the hose became brittle at the cold temperature. As the temperature went up, the pressure in the hose increased and gas penetrated through the hose. Tygon tubing was being used in the first prototype. In order to continue the test, the hose was reinforced with meshed wire and this was found to be satisfactory. To ensure the integrity of the argon supply system, polyurethane tubing with a temperature rating of -60°C to 115°C was selected for the successive units.

b. The circuit breaker of the graphite furnace power supply tripped when operating at 57°C. Successive measurements showed that the supply can be operated at 57°C with 110 V ac input and about 40°C with 220 V ac input. A series of experiments have been conducted to investigate the cause. It appeared that the cause was due to the junction temperature of the SCR device in the GFPS being hot and close to its limit. When operated at 220 V ac mode, the voltage gradient (dv/dt) was twice that of the 110 V ac mode. The high voltage gradient caused the SCR to mistrigger, which in turn, caused a high current surge and this tripped the circuit breaker. A different type of SCR was selected for the successive units and the temperature performance was satisfactory.

c. The test was continued by operating at 110 V ac input. The PWMA executed the atomization cycle correctly, but failed to print out the data in the analysis mode. Ten test samples and three calibration samples were processed in the calibration mode where raw data were printed out. The concentrations of these test samples were then calculated using the data from the three calibration samples and they are presented in the data sheet. The temperature was lowered to 50°C and the unit functioned properly. These tests indicated that one of the EPROMs containing the calculation routine might have malfunctioned at 57°C ambient. The EPROM has a temperature rating of 70°C for the case temperature. When operating at 57°C, the case temperature is approximately 70°C with the cooling fan turned on. Military parts with higher temperature rating can be obtained. However, the price is about four times that of the commercial parts. As a result, for the

successive five units, the circuit boards are facing upwards and the spacing between the microprocessor board and other boards is increased to facilitate cooling.

d. The regulator for the sample injection gun failed to regulate gas pressure after remaining at 57°C for an hour. The regulation adjusting knob was activated several times and the regulator was returned to normal operation. The regulator used in the first prototype has a range between 0-125 psi and the argon pressure for the sample injection gun was set at 4 psi. It is rationalized that the regulator, spring tension, which drives the stem to open and close the regulator, is very small and can fail to open. For the successive five units, a regulator with 0-10 psi range is used. The spring tension setting is then 40% of the total adjustment and should alleviate the problem.

e. Electrometer outputs were measured at 57°C and the readings were compared with those taken at ambient temperature. All the channels have lower outputs, which are mainly due to the decrease in gains of the photomultipliers. However, the absorption signals are not significantly affected by the decrease in electrometer output. This is because the atomic absorption signal is the ratio of the light intensities before and after the absorption and is not affected by the absolute intensity change.

In summary, the temperature test revealed some component problems in the system. Fortunately, there was no permanent damage to the system. The unit performed well after returning to ambient temperature. Problems found were corrected in the successive five units.

4.4 HUMIDITY TEST

The PWMA was placed in the P-E humidity chamber, as shown in Figure 18, and the chamber was operated at its maximum capacity (95%). Due to the accuracy of the measurement device, it was not certain whether the 95% relative humidity had been reached or not. However, the chamber was operated at 102°C and the

relative humidity reading was 85%, therefore, the water content in the chamber was much higher than the water content of 100% relative humidity at ambient temperature.

Three test samples were injected after the unit was stabilized in the humidity chamber for four hours. The data were repeatable. However, after opening the chamber to inject the sample, the equilibrium in the humidity chamber was disturbed and the relative humidity at that instant might have changed slightly. The unit was returned to room ambient and the accuracy test was repeated. There was no change in performance.

4.5 INCLINATION TEST

The purpose of the inclination test is to determine whether the PWMA can be set up and operated on a sloping hill. The furnace-optics container was tilted to 15 degrees in the direction perpendicular to the axis of the graphite tube. The result was found unsatisfactory because the oil sample flowed toward one side of the tube. It is therefore recommended that when operating on a slope, the furnace-optics should be oriented so that the tilting is in the direction parallel to the axis of the graphite tube.

4.6 FINAL FUNCTION TEST

After all the environmental tests were completed, the first prototype unit was returned to the laboratory and a function test was performed using 110 V ac. The data is shown in Appendix A. Also, after each environmental test, accuracy tests for 10% and 70% samples were performed. The data from these tests are compiled in Table 2. The result shows that the accuracy and long term reproducibility for most of the elements are good, except for Mg and Al at high concentrations.

TABLE 2. Compilation of Accuracy Data for 10% and 70% Levels

	Calibration Standard (ppm)	Measured Concentration								Deviation From Actual (ppm)	Standard Deviation (ppm)
		1	3	3	4	5	6	7	Ave		
Ag	1	1	1	1	1	1	1	0	0.9	0.1	0.38
Al	5	6	4.2	4.8	5	3.8	6	6.8	5.2	0.2	1.1
Cr	1	1	1	1	1	1	1	1	1	0	0
Cu	4	4	3.2	5	4.6	2.6	4.8	2	3.7	0.3	1.2
Fe	10	12.6	10.6	12	11	10	11.2	9.4	11	1	1.1
Mg	5	3.4	3.4	4.2	5.8	5.8	4	3	4.2	0.8	1.1
Ni	3	5.4	4	3.2	4	4	3.4	2.8	3.8	0.8	0.83
Si	2	2.4	2.6	2.2	1.1	1.2	2	2.4	2.1	0.1	0.46
Ti	2	3	2.6	2.2	3	2.8	1.2	3	2.5	0.5	0.66
Ag	7	7	6	7	7	7	6.6	7.2	6.8	0.2	0.41
Al	35	32.4	15.2	26.6	11.6	17.4	31	26.4	22.9	12.1	8.1
Cr	7	6.4	6.6	7.2	6.6	7.2	7.2	7.2	6.9	0.1	0.36
Cu	28	24.8	24	26.8	26.4	26.8	27.6	27.4	26.2	1.8	1.4
Fe	70	73.6	65.8	78	75.2	73.8	75.4	76.6	74	4	3.9
Mg	35	16.2	18.8	28.8	38.6	31.2	28.4	38.2	28.6	6.4	8.6
Ni	21	21.6	20.6	22.6	22	22.4	22.4	21.6	21.9	0.9	0.69
Si	14	17.6	13.8	10	16.6	9.8	8.2	9	12.1	1.9	3.8
Ti	14	20.6	15.2	14	15	15.2	11	15.2	15.1	1.1	2.8

1. Performance Test
2. Post Shock Test
3. Post Altitude Test
4. Post Thermal Test
5. Post Humidity Test
6. Thermal Test
7. Final Functional Test

NOTE: Each data point is the average data of 5 samples.

CHAPTER V
FIELD TEST PROTOTYPES

5.1 SUMMARY

A total of five field test prototypes were constructed after completing the design evaluation test of the first prototype. Modifications were made to improve the analytical performance and the manufacturability of the PWMA. Major modifications included changes to the polychromator slits, the graphite furnace power supply, and the overall package.

5.2 POLYCHROMATOR SLITS

In the five field test prototypes, narrower exit slits are used and the spectral bandpass for most of the channels are 0.2 nm. Considerably wider exit slits were used in the first prototype. The intent for using wider slits was to measure the non-absorbing lights from the second HCL as background correction lights for the elements in the first HCL. This scheme is described in Paragraph 3.1. However, the wider slit also allows the unwanted radiation from the first HCL itself to enter the detector. The presence of unwanted radiation would limit the absorbance that can be obtained, which in turn causes curvature in the calibration curve. Since the background correction was found to be unnecessary, as described in Paragraph 3.1, slits are narrowed to eliminate the unwanted radiations.

5.3 GRAPHITE FURNACE POWER SUPPLY

The silicon controlled rectifier used in the first prototype was manufactured by Brown Boveri (BCC Model MRR50). The voltage gradient, dv/dt, rating for this type of SCR is 200 V/μs at a junction temperature of 125°C. As discussed in Paragraph 4.3.2, the SCRs failed during the high temperature test of the first prototype. The cause was that the voltage gradient exceeded the rating at elevated temperature. SCRs with such a high current switching capability and compact size are not common. Fortunately, a different type of SCR was available

recently from the same manufacturer. This type of SCR, Model CSR147, has a dv/dt rating of 1000 V/ s at 125°C, which provides a relatively large safety margin. This type of SCR has been tested at an operating temperature of 70°C and above, without failure. With this new SCR, the controlled output of the graphite furnace power supply can reach approximately 520 amperes with the specified power input limit.

5.4 PACKAGE

5.4.1 CONTAINER. A larger container, 18 inches x 18 inches x 10.5 inches is used for the field test prototypes. The larger container greatly reduces the difficulty of installation, thus saving the labor for assembling the PWMA. In the furnace-optics container, a larger space is provided between the honeycomb plate and the container wall so that a thicker (0.5") shock absorber can be used for shock isolation. Also, in the E-A container, retaining screws with thumbnuts are used so that front panels can be removed easily. The tradeoff for this larger container is the weight increase of about three pounds each.

5.4.2 SAMPLE INTRODUCTION DEVICE. The sample gun has been redesigned with emphasis on human engineering. Wooden models, with different handles, were made and passed to different people for evaluation. The final shape is shown in Figure 19. The included angle between the tip and the handle is smaller than 90 degrees to facilitate the insertion of the tip into the graphite tube. This sample gun has been proved to be easy to use and to be repeatable.

5.4.3 GRAPHITE FURNACE ASSEMBLY. The mounting of the graphite furnace has been modified. An argon interface manifold is mounted on the furnace mounting bracket. All the argon plumbing originating in the furnace is connected to one side of the manifold. The furnace assembly can then be removed by removing the manifold and the mounting screws.

A new left-hand window was designed so that the window can be removed vertically. This allows the cleaning of the window without having to remove the furnace.

5.4.4 GRAPHITE FURNACE POWER SUPPLY. Components of the graphite furnace power supply have been rearranged to accommodate the new type of SCRs. The SCRs are clamped between copper heat sinks, upon which the cooling air is ducted. Clamping force, as high as 1000 pounds, is applied to provide an efficient heat conduction, as well as a good electrical contact. With this arrangement, the temperature of the SCR only rises about 5°C above ambient at the end of the atomization cycle. This efficient cooling also allows the furnace duty cycle to be increased, e.g., shorten the analysis cycle when the water cooled furnace is used.

CHAPTER VI
TEST RESULTS

6.1 SUMMARY

Test results discussed in this chapter are the data obtained from the design verification tests. Design verification tests were intended to demonstrate that the PWMA would meet the performance requirements as well as the environmental requirements. Tests for the first prototype were conducted by the author in July, 1984; tests for the second prototype were performed by the USAF project engineer in May, 1985; tests for S/N 003, S/N 004, and S/N 005 were tested by the author on the same day as that of S/N 002, with three units set in the same lab; tests for S/N 006 were performed by another engineer at a later date. Test data were calculated and are tabulated in Appendix A.

To summarize, Fe, Ag, Cu, Cr, Ni, and Ti performed well; Mg, Al, and Si have deficiencies in different areas. Possible improvements of these areas are discussed in the next chapter. Also, there were no obvious differences in performance from unit to unit, except for unit S/N 001. The differences in data among units are primarily caused by the calibration of that run, and possibly human errors at certain sample injections.

6.2 TEST SAMPLES

The test samples used in the design verification test were prepared from the CONOSTAN metallo-organic standards except for the particle size testing. Multi-element standards were obtained by mixing single element CONOSTAN standards into engine oil to make the required concentrations. For simplicity, the metal concentration in all the test samples are expressed according to their full scale ranges. For example, a 50% sample contains 50 ppm of iron, 5 ppm of silver, 25 ppm of aluminum, 20 ppm of copper, 5 ppm of chromium, 25 ppm of magnesium, 15 ppm of nickel, 10 ppm of silicon, and 10 ppm of titanium. The percent of the full scale will be the nomenclature used throughout this report.

Originally, it was intended to use oil meeting MIL-L-6082 as the base oil for the calibration standards. However, it was found that to use MIL-L-7808 oil as the calibration oil for analyzing MIL-L-7808 samples gave more accurate results. Since most of the aircraft of the USAF use MIL-L-7808 oil, it was decided to use the MIL-L-7808 oil for calibration.

6.3 PERFORMANCE TEST

6.3.1 DYNAMIC RANGE

Five replicates of 90% and 100% samples were analyzed and their mean values were compared to show that the test samples did not saturate the PWMA detection capability at these high concentrations. Most of the discrepancies were caused by variances in calibration; their remedies are discussed in Paragraph 7.1.

a. Ag, Fe, Cu, and Ni performed well at the high concentrations as shown in Table 12 (Appendix A).

b. The result for Cr at 90% was distinguishable from that of the 100%, but the results for both samples are low compared to the true values.

c. The results for Si and Ti at 90% were distinguishable from that of the 100%, but the results were higher than the true values. Titanium also showed some memory effect at these high concentrations and this effect is discussed in Paragraph 7.6.3.

d. For Mg and Al, although the data for 90% and 100% were distinguishable, data were inaccurate at these high concentration levels.

6.3.2 ANALYSIS TIME

The overall analysis cycle takes 4 minutes. The atomization cycle takes 55 seconds and the printer starts to print about 75 seconds after the atomization cycle is completed. During this period, the microcomputer converts all the optical signals to absorbance values, sums the point absorbance value independently for all nine elements, and calculates concentrations using the calibration curves. The computation process is slowed by the calculation of the

logarithmic function. However, faster microprocessors can be used to speed up the data processing time.

Fifteen samples can be analyzed in an hour. This was demonstrated by analyzing 15 samples, consecutively, during the repeatability test.

6.3.3 DETECTABILITY

Five replicates of 1 ppm multi-element samples and blank samples were analyzed and compared to show that the 1 ppm detectability is achievable. Test results are summarized in Table 13 (Appendix A).

a. All the elements showed 1 ppm detectability except Si where the detectability was about 2 ppm. This resulted from the compromised atomization cycle for detecting other elements.

b. In the first prototype, the test result for Ni was high, which was due to the error of the calibration curve at the low end. This problem has been corrected with the new polychromator as demonstrated by the test results of units S/N 002 through S/N 005.

6.3.4 ACCURACY

Five replicates of 10%, 40%, and 70% samples were analyzed and their mean values were compared to the true values. Test results are summarized in Tables 6 through 8 (Appendix A).

a. All the elements performed well at 10% range, except Al. The problems associated with Al are discussed in Paragraph 7.6.4.

b. In the first prototype, Ti showed high results at 70% level. The results were improved in the subsequent units by improved graphite furnace power supply and correction algorithm.

c. Mg and Al showed low results at the 40% and 70% levels. This is primarily caused by the saturation problem and the calibration curve as discussed in Paragraph 7.2.

d. Accuracy tests of Mg and Al with reduced full scale range are shown in Tables 9 through 11 (Appendix A) and the accuracies are improved.

6.3.5 REPEATABILITY

Fifteen replicates of 10% and 50% were analyzed and their standard deviations were calculated to demonstrate the repeatability. Test results are summarized in Tables 4 and 5 (Appendix A).

a. The standard deviations for all the elements at the 10% concentration level were within 1 ppm, except for Al in a few units. The standard deviations for Ag and Cr were zero for most of the tests.

b. The standard deviations for Ag, Cr, Cu, Fe, Ni, and Ti were better than 1 ppm or 2.5% of the full scale at the 50% concentration level with a few exceptions.

c. The standard deviations for Si were about 2 ppm at the 50% concentration level.

d. The standard deviations for Mg and Al fluctuate, depending on that particular run. This is because the errors were amplified by the calibration function. The causes and the corrections are discussed in later paragraphs.

6.3.6 PARTICLE SIZE INDEPENDENCY

Test samples for the particle size independency were furnished by the Air Force in July, 1983. Single element particles ranging from 10 to 20 micrometers were dispersed in MIL-L-7808 oil. All the samples were ultrasonically vibrated for an hour and handshaken prior to introduction into the furnace. Test results with S/N 001 are tabulated in Table 14 (Appendix A).

a. The concentrations measured were compared to the actual values, and the ratios had a range from 40% to more than 100%, except Cu.

b. The sample acquisition time for Cu can be extended for better particle analysis and this has been incorporated into all the units.

c. Dense metals such as Fe and Ag are difficult to blend into the oil; therefore, test samples must be mixed very well prior to sample introduction.

In general, analytical techniques such as flame AA and atomic emission fail to detect particles larger than a few micrometers and the exact cut-off would depend on the literature referenced. The limitation is due to the sample introduction method used and to the low sample residence time associated with the excitation processes. For furnace AA, the sample residence is relatively long so that particles up to 20 micrometers can generally be atomized[4]. Unfortunately, elements in the PWMA were not atomized at their optimum temperatures, thus limiting large particle detection. However, the atomization cycle can be extended to improve the particle size detectability.

Another limitation that statistically affects the particle size detection is related to the sample introduction. As an example, silver has a specific gravity of 10.5, and for a spherical particle with a diameter of 20 μm, the weight is 44 ng. For a sample size of 8 microliters, this quantity is equivalent to 5.8 ppm. The full scale range of silver is 10 ppm and this range will be exceeded if there are two such particles in the oil. This is a statistical limitation and no practical method can be used to improve the analysis.

6.3.7 SAMPLE COMPOSITION

Five replicates of 20%, 50%, and 100% samples prepared in MIL-L-6082 oil and MIL-L-23699 oil were analyzed with S/N 003 and the results are tabulated in Table 15 (Appendix A).

a. Results obtained from the MIL-L-23699 oil were comparable to the actual concentrations.

b. Results from the MIL-L-6082 oil are lower than the actual concentrations. This is caused by the volume difference in dispensing the MIL-L-6082 oil and the MIL-L-7808 oil. A possible correcting method is to use a larger tip for analyzing the MIL-L-6082 oil to compensate the difference in volume.

6.3.8 ENVIRONMENTAL TESTS AND POST ENVIRONMENTAL TEST

For the environmental and post environmental tests, five replicates of 10% and 70% samples were analyzed and their mean values were compared to the actual values to show that there was no degradation after the environmental tests.

a. The accuracy data for seven different situations are shown in Table 2 (Chapter IV).

b. There was no obvious degradation in performance after the environmental tests. The variations observed are primarily caused by different graphite tubes and different calibration runs.

c. Test results obtained at 57°C were essentially the same as those obtained at ambient temperature.

6.3.9 FINAL FUNCTIONAL TEST

Final functional tests of S/N 001 were performed using 110 V ac. The detectability, accuracy, and repeatability tests were repeated.

a. The concentration data for 1 ppm Ag showed zero ppm. The Ag concentration was calculated to be 0.35 ppm by using the absorbance data through a separate run. The 0.35 ppm was rounded off to zero during the concentration calculation. The 1 ppm detectability is demonstrated by S/N 002 through S/N 005.

b. The 1 ppm Ti was not detectable; because the peak current supplied by the GFPS at 110 V is lower than that of 220 V, the sensitivity of Ti is thus lower. For units S/N 002 through S/N 005, a new power supply is employed and the peak current can be controlled as long as the input voltage is within ±15% of the specified 115 and 230 V.

c. The accuracy data were about the same as that obtained with 220 V input.

d. The repeatability data for the 10% level were the same as that obtained with 220 V input.

e. The repeatability data for the 50% was worse than that obtained with 220 V input. By carefully examining the data, there were two bad runs which might be due to bad injections or bad sample tips. By eliminating these two runs, data were about the same.

6.4 PERFORMANCE BY ELEMENTS

This section summarizes the data obtained for each element from units S/N 001 through S/N 006. The problems associated with the analytical performance and methods of improvement are discussed in Chapter VII.

6.4.1 IRON

Iron performs fairly well. Accuracy and repeatability are good, considering the large dynamic range of Fe. The variations are caused by the sample introduction error and the atomization variation. The recovery of particles in the size range of 10-20 micrometers is about 60%.

6.4.2 SILVER

Silver is the most reproducible element. The standard deviations are zero for most of the cases. The accuracy is good. Since Ag is a dense element, large particles tend to settle and the sample must be mixed well before introduction.

6.4.3 CHROMIUM

Chromium is also very reproducible. The full scale range of chromium is 10 ppm and chromium is also a dense element. The statistical limitation of large particle detection of chromium is similar to silver.

6.4.4 COPPER

Copper is very reproducible. Extending the sampling time would improve the particle detectability.

6.4.5 NICKEL

In S/N 001, nickel tended to saturate at high concentrations. However, after modifying the polychromator with a narrower exit slit, the calibration curve became linear and the data became very accurate.

6.4.6 TITANIUM

Titanium became reproducible after a new graphite furnace power supply was employed. It still has slight memory effect. The cause and possible corrections are discussed in Paragraph 7.6.3.

6.4.7 MAGNESIUM

Magnesium is reproducible at lower concentrations. At higher concentrations, the signal tends to saturate and the error is amplified. A possibility is to reduce the full scale range and accept some inaccuracy at high concentration or to do dilution if the sample concentration exceeds the calibrated range as detailed in Paragraph 7.5

6.4.8 ALUMINUM

Aluminum suffers the same saturation problem as Mg. The solutions are discussed in Paragraph 7.6.4.

6.4.9 SILICON

Silicon is the most difficult element to analyze because of losses during the burn cycle. One way to improve the performance is to increase the calibration range so that calibration points are more reproducible which minimizes the errors introduced by calibration. Also, Si sometimes produces erratic results. It is not clear whether this is coming from the contamination or other sources. This should be examined carefully in the future.

CHAPTER VII
DISCUSSION

7.1 SUMMARY

Data obtained from the prototypes have revealed a number of parameters which are important to the PWMA. The effects of these parameters and the improvement of analytical performance are discussed in this chapter.

A graphite furnace atomic absorption instrument has been used as a single-element laboratory instrument for over a decade. In laboratory operation, the operator has the freedom to adjust the instrument parameters and the sample concentration for different applications. The PWMA is developed to be a fixed monitoring instrument. It analyzes nine elements in one cycle, using an undiluted oil sample. Therefore, parameters such as tube variation and sample concentration, although less important to lab AA instrument, have significant impact to the PWMA and these parameters are discussed. Finally, tradeoffs among analytical performance, JOAP requirements, and simplicity of operation must be carefully considered.

7.2 CALIBRATION

The concentration data printed out by the PWMA are calculated by the microprocessor with the use of a calibration technique. Samples with known concentrations are analyzed first and the absorbance data obtained are used to construct calibration curves. Absorbance data obtained from unknown samples are then compared to the calibration curves so that their concentrations can be calculated. The calibration is the most important operator controlled factor in the PWMA operation. An inadequate calibration would affect the results for all the analyses using that calibration. Typical calibration curves using absorbance data from S/N 002 are plotted in Figure 19.

As shown in the figure, most of the curves have curvature at high concentration levels. Nonlinear calibration functions are required to provide better fitting of data. In PWMA, three calibration standards at 20%, 50%, and 100% plus a

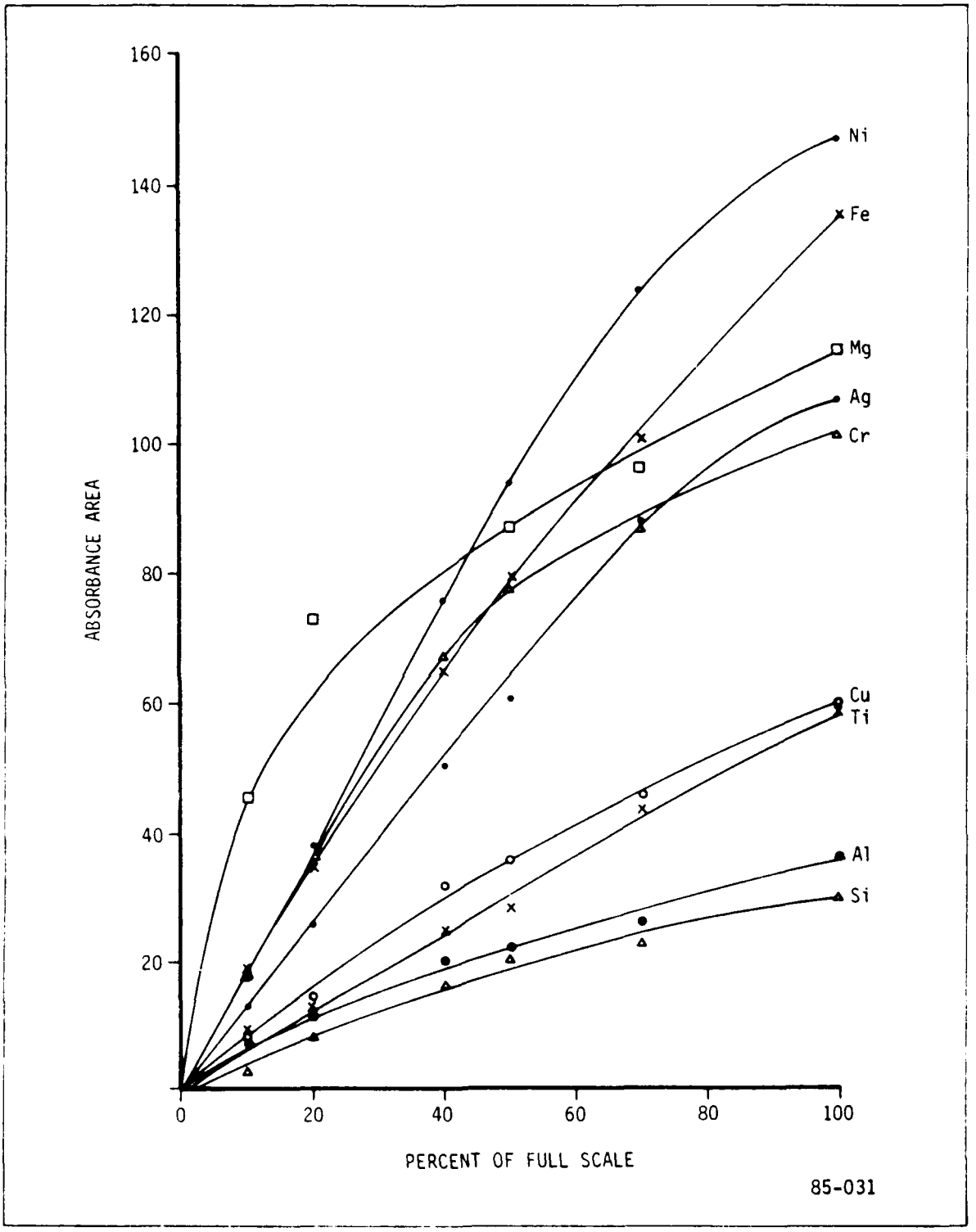

FIGURE 19. Typical Calibration Curves

blank (0%) are used. A pair of two point rational equations[5] are used to fit data for all nine elements. The equation has the form:

$$C = \frac{K_1 A}{K_2 A - 1}$$

The first part of the curve uses absorbance values obtained from 0%, 20%, and 50% samples and the second part of the curve uses values obtained from 0%, 50%, and 100%. The computer selects the proper curve to calculate data depending on the absorbance value of the unknown sample. Nine sets of these curves are used for calculating concentrations of all nine elements. In principle, using a three point calibration equation to construct one calibration curve would provide the optimum fitting. However, it has a higher possibility for obtaining erratic results, i.e., if a data point is off, the calibration equation might create a non-smooth curve to pass the three calibration point, which causes an even larger error.

To design a good calibration equation to fit all nine elements for the PWMA is not a trivial task. An ideal calibration equation should be accurate for all the concentration ranges, have enough flexibility to cope with absorbance variations of different graphite tubes, and be less susceptible to human errors. The present calibration scheme is a compromise of the above conditions. A possible improved method is to use a weighted nonlinear least square fit with four calibration standards. The least square fit should be more immune to errors and variations. It is anticipated that the field evaluation data would provide information on the range of variation so that an optimum equation can be designed for future units.

7.3 GRAPHITE TUBE VARIATION

Due to the complexity of the atomization cycle, the reproduction of the same temperature profile from tube to tube is critical. The PWMA graphite furnace power supply is current controlled so that any change in the graphite tube's resistance would result in a different temperature profile. If the temperature change is large, it will cause either saturation or loss for certain elements.

In this development program, standard pyrolytically coated graphites were purchased and modified for PWMA use. The modification is to enlarge the

aperture of the tube (from 0.07" to 0.1") in order to accommodate the PWMA's sample introduction tip. The drilling process breaks the pyrolytical coating at the aperture. It is uncertain whether this process would affect the characteristic or not. However, for large quantities, tubes with modified aperture size can be made by the tube manufacturer, thus ensuring a better quality of the tubes.

Several schemes that can possibly improve the temperature reproducibility are discussed below. Some of them are currently under study.

- o Use power control for the GFPS instead of current control.
- o Mount a pyrometer in the back of the graphite furnace to actually monitor the tube temperature. A small pyrometer (0.5" Dia. x 2") is commercially available. However, this would increase the production cost of the instrument.
- o Introduce a standard sample based on the absorbance value obtained. The computer will judge the temperature profile for that tube and change the control current accordingly.
- o Tightly control the quality of the tube so that variations are kept minimal.

7.4 ATOMIZATION CYCLE

An ideal multi-element atomization cycle should provide optimum atomization conditions for each element. However, each element has its own characteristics and optimum atomization conditions between two elements might not be compatible. The PWMA atomization cycle was developed by characterizing each element first and then combining the atomization conditions of nine elements together. Inevitably, tradeoffs must be made and, in some cases, the tradeoff affects the performance.

The tradeoff between silicon and the other elements is the most difficult one. Silicon has an atomization temperature of 2700°C and is measured at the last step of the atomization cycle. However, silicon starts to lose at about 2000°C.

Therefore, the onset of atomization of other elements such as Mg, Cu, Fe, Ni, and Cr has to be kept below 2000°C, which affects the atomization of these elements. Furthermore, this temperature setting is critical so that the atomization cycle is more susceptible to temperature (tube) variation.

In present JOAP guidelines, silicon analysis is not required for most of the aircraft engines although foam problems in F-15 and A-7 aircraft require silicon monitoring. It is important for ground equipments and helicopters. For PWMA, the frequency of analyzing silicon is probably low. Therefore, it would be beneficial to set up the silicon analysis in a different atomization cycle, activated by a separate switch. This tradeoff would not only improve the performance of the other elements mentioned above, but also make the atomization cycle less susceptible to temperature variations.

7.5 DYNAMIC RANGE

Graphite furnace AA is a very sensitive technique. Efforts were made to reduce the sensitivity to meet the full scale requirements of the PWMA. Also, the absorbance is a logarithmic function. In simplified form, $A = \log I_o/I,$, where I_o is the transmitted light intensity and I is the reduced intensity after absorption. This logarithmic nature limits the linear range of the absorbance. For the PWMA, a still further difficulty is to adjust the sensitivities of all nine elements so that they would fall into a reasonable linear working range.

From the calibration curves shown in Figure 19, Mg and Al have severe curvatures at high concentration ranges. Within these ranges, a small fluctuation in the instrument response will result in a large error in concentration data. The error will become even larger if the sensitivity of the tube drifts after a certain number of samples have been analyzed. The reslope (one point calibration) discussed in Paragraph 2.9.1, would not be able to correct the data effectively.

To assess the possibility of reducing the full scale requirements for Mg and Al, wear metal frequency distribution data from the USAF aircraft for the year of 1983 were examined. Selected data from twenty types of aircraft with abundant test data are tabulated in Table 3. The table summarizes the total occurrences

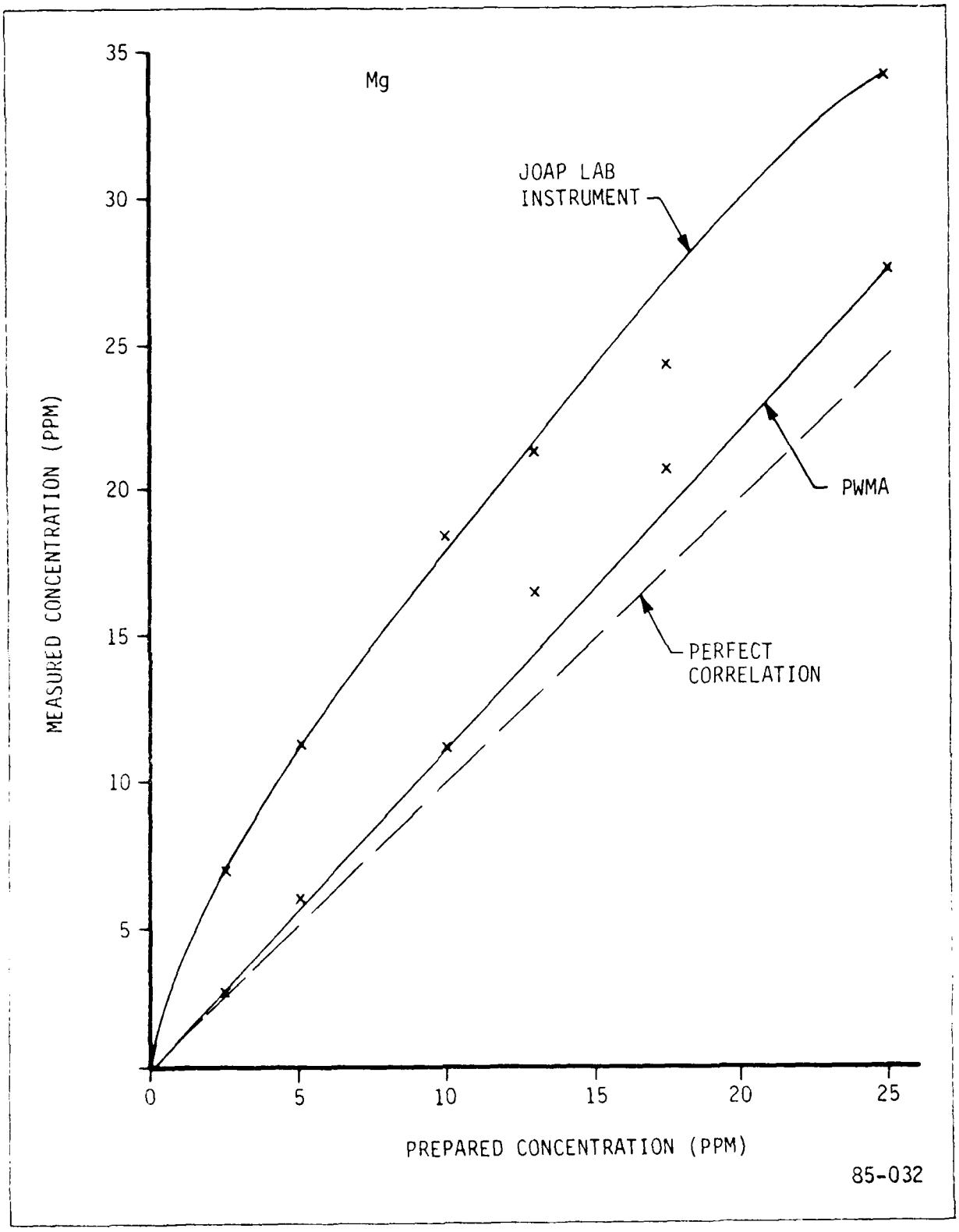

FIGURE 20. Correlation Data of Magnesium

TABLE 3. Wear Metal Frequency Distribution*

Equipment/ End Item Model	T-33A J33-35	B-52G J57-43	Kc-135A J57-59	Kc-135Q J57-59	T-39A J60-3	T-37B J69-25	F-106A J75-17	F-4G J79-8	F-4C J79-15	RF-4C J79-15
Total Samples	11,525	14,458	22,142	2,042	9,132	39,150	15,886	10,633	33,000	37,039
Freq. of Mg - 25 to 50 ppm	0	55	22	5	10	1	5	1	5	16
Freq. of Mg - 50 ppm	2	12	5	3	4	2	4	24	4	25
Freq. of Al - 25 to 50 ppm	0	1	1	0	0	1	0	0	0	1
Freq. of Al - 50 ppm	1	1	0	0	2	0	0	0	2	2

Equipment/ End Item Model	F-4D J79-15	F-4E J79-17	T-38A J85-5	F-5E J85-21	F-15C F100-100	F-15A F100-100	F-15D F100-100	F-16A F100-200	F-111A TF30-3	F-111E TF30-3
Total Samples	53,584	75,579	73,724	15,985	40,623	117,263	18,373	41,970	13,026	10,405
Freq. of Mg - 25 to 50 ppm	5	25	32	0	3	2	0	2	14	0
Freq. of Mg - 50 ppm	29	67	152	14	106	310	10	41	10	0
Freq. of Al - 25 to 50 ppm	0	0	0	0	0	0	1	0	0	0
Freq. of Al - 50 ppm	0	11	171	3	7	126	0	83	6	0

*Data are selected from heavily used aircraft during 1983 with a total number of 655,539 samples.

of Mg between 25 ppm and 50 ppm and the total occurrences greater than 50 ppm. From 655,539 test data, the occurrences for having Mg greater than 25 ppm is about 0.15%, which is a very small fraction of the total. The frequency distribution of Al is also tabulated.

The data of the frequency table were obtained from atomic emission instruments presently used in the JOAP base laboratories. The emission instrument suffers from inter-element and matrix interferences, so that the data obtained were different from the true values[6]. The ratio between the analyzed value and the true value may vary from element to element and even vary for different concentrations. Preliminary correlation data of Mg between the PWMA and the JOAP lab instrument obtained from JOAP TSC is shown in Figure 20. It indicates that 35 ppm reading on the lab instrument corresponds to about 25 ppm of the PWMA reading. The ratio of lab instrument reading versus PWMA reading varies from 2.4 at lower concentration regions to 1.4 at higher concentration regions. These data are consistent with the table for conversion [7] of lab instrument readings into flame AA instrument readings.

From the frequency data, it is proposed that the full scale range requirement for Mg and Al be reduced. In the situation where a high result is shown in the analysis, the sample can be diluted and re-analyzed. Since PWMA can analyze oil samples directly, the sample can be diluted with blank MIL-L-7808 oil and no chemical solvent is needed.

In general, the PWMA has the best accuracy at the low ppm region where the calibration curves are linear. By closely examining the frequency distribution data and the JOAP guidelines, wear metal concentrations for a majority of the JOAP samples are in the low ppm region. For example, when the Fe level of an F-15 aircraft engine reaches 15 ppm, the engine is considered as abnormal. For heavier aircraft such as the B-52, the abnormal level for Fe is about 40 ppm. These two levels correspond to about 5 and 20 ppm of PWMA readings as shown in Figure 21. These guidelines indicated that the PWMA should focus on the accurate analysis of lower concentration levels. It is therefore proposed that the PWMA calibration should include 4 standards; three of them focused at

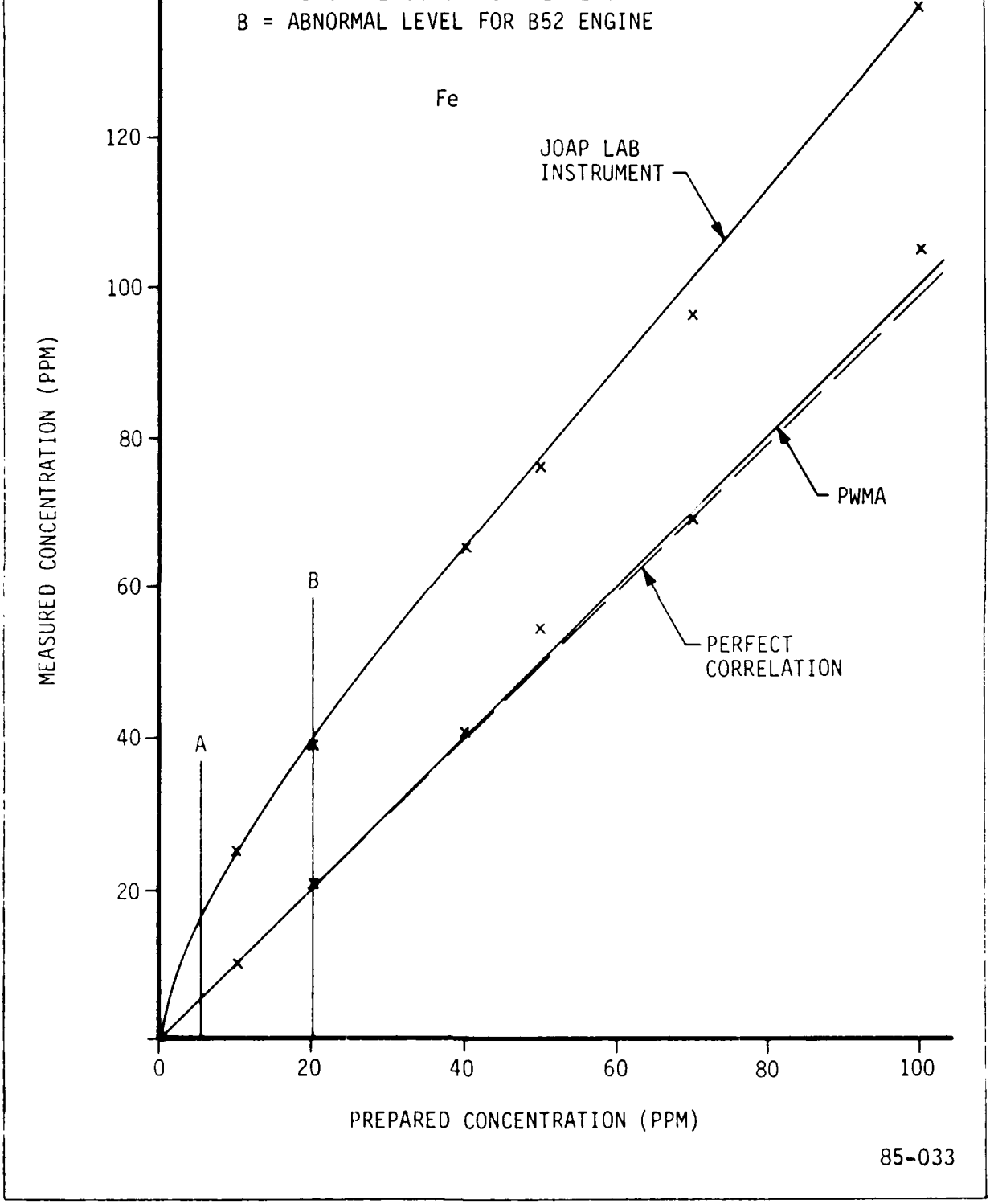

FIGURE 21. Correlation Data of Iron

the lower end of the full scale ranges to gain maximum accuracy and accept some variations at high concentrations. The actual concentrations of calibration points can be assessed with the aid of field test data.

7.6 OTHER AREAS OF IMPROVEMENTS

The following subsections describe some areas where improvements are recommended. However, due to time constraints, these improvements were not incorporated into the prototypes.

7.6.1 TEMPERATURE CONTROL

Air cooling has been used to cool the graphite furnaces for all the prototypes. At the end of the four minute analysis cycle, the graphite furnace is about 20°C above ambient. After five consecutive analyses, the furnace temperature at the end of the analysis cycle is about 30°C above ambient, and reaches equilibrium. The initial temperature difference between the first sample and the successive samples affect the temperature profile of the atomization cycle, which in turn affects the repeatability. This problem can be resolved by temperature controlling the furnace to a fixed temperature, e.g., 60°C, thus eliminating the initial temperature difference between analyses. The temperature control has an added advantage of reducing the analysis cycle time. For the prototypes, the cool down time from the end of the atomization cycle to 60°C is about 1.5 minutes with 22°C ambient. With this temperature control scheme, the analysis time can be reduced to 2.5 minutes. Furthermore, the present PWMA furnace is a modification of a standard water cooled furnace. Copper-beryllium pins are used as heat sinking devices. Unfortunately, areas around the graphite contact rings are surrounded by hollow water pipes and the cooling pins cannot be attached. The heat dissipation is therefore somewhat inefficient. The efficiency can be improved if the furnace is designed for air cooling only and if the water pipe is replaced with solid metal.

If water cooling is used, the cool down time for the furnace to return to water temperature is less than 20 seconds. This initial temperature difference problem automatically goes away and the analysis speed is increased. The tradeoff would be the efficient cooling with water versus the convenience of using air cooling.

7.6.2 SAMPLE INTRODUCTION

The sample introduction device developed in this program has a repeatability better than 1.5%, measured gravimetrically. Since the oil sample is expelled by the argon pulse, to maintaining a constant pressure of the pulse is critical. During the testing of prototypes, output pressure variation caused by the regulator has been found in several occasions; that is, after the sample gun has been setting for a long period of time, the pressure builds up and the pressure relief mechanism of the regulator fails to relieve the pressure. This causes sample introduction error; a better quality regulator should be evaluated. An alternative is to mount a pressure gauge in a visible area so the operator can constantly check the sample injection pressure.

7.6.3 TITANIUM MEMORY

Titanium exhibits some memory effect, which is presumably due to titanium's high boiling point and carbide formation characteristics. One method to reduce the memory is to extend the time of the clean cycle. Unfortunately, the long clean cycle tends to shorten the graphite tube life. A compromise method is to introduce a separate clean cycle. Once a high concentration of titanium is shown, the operator should start the clean cycle to clear the memory.

7.6.4 ALUMINUM IMPROVEMENT

The repeatability of aluminum is poorer than the other elements, even for 10% samples. This is primarily caused by peak integration error. In the initial design, 150 data points are allocated for each element. Since the HCL is modulated at 40 Hz, 150 data points correspond to 3.75 seconds of peak integration time where 40 points per second are sampled. If the peak integration time is longer than 3.75 seconds, the computer has to skip data points during the sampling, i.e., 20 points per second if the integration time is between 3.75 seconds to 7.5 seconds. For the present atomization cycle, the integration time of aluminum is 4 seconds, which includes two sharp peaks, one presumably from aluminum oxide. Integration error occurs because only 20 points per second are sampled. This error can be minimized by increasing the data points allocated to aluminum, e.g., change the total data points sampled to 160 so that 40 data

points can be sampled per second. Another possible improvement is to detect aluminum at 308 nm, but this requires a change in the polychromator arrangement.

7.6.5 PRINTER

A thermal printer manufactured by Datel is used in the PWMA. The printer is compact, reliable, 110 V/220 V switchable, and is able to operate within the temperature extremes. However, it was found that the MIL-L-7808 oil reacts with the thermal paper and smears the printout. Several commercially available thermal printers and papers from different manufacturers were examined and all of them were affected by the MIL-L-7808 oil. Other types of printer papers, such as those used for impact printers and discharge printers, are not affected by the MIL-L-7808 oil. However, the tradeoffs are cost, size, and reliability. It seems to be more practical to use the same printer, but to exercise greater caution not to contaminate the paper with oil.

Recent discussions with one of the paper manufacturers indicates that one possible solution is to coat the paper with protection coating, which is at the expense of higher cost.

CHAPTER VIII
CONCLUSIONS

A total of six prototype PWMAs have been constructed and tested. Preliminary data have demonstrated the capability of meeting the needs for oil analysis during deployment. Major achievements of the program include:

a. Developed a multi-element analysis scheme to routinely analyze nine elements with one oil sample. This is believed to be done for the first time in graphite furnace atomic absorption instrumentation.

b. Developed a miniaturized graphite furnace power supply weighing 15 pounds, capable of delivering 520 amperes controlled current. The power supply can be switched for either 110 V or 220 V operation. A commercial equivalent would weigh approximately 100 pounds.

c. Developed a novel sample introduction device capable of sampling MIL-L-7808, MIL-L-23699, and MIL-L-6082 oils directly. The repeatability for sampling MIL-L-7808 oil is better than 1.5%.

d. Designed a compact nine channel polychromator with 1 A resolution. The polychromator can maintain its stability within ±35°C temperature span.

e. Designed an air cooled graphite furnace while the water cooling capability is still maintained.

f. Packaged the instrument in a portable and ruggedized version

g. Designed for simple operation. The analysis cycle is accomplished by one pushbutton operation.

To improve the combat readiness for the US aircraft in forward bases, the deployable oil analysis instrument is an indispensable tool. The successful development of the PWMA not only relieves the logistics burden during deployment, it also provides a fast, simple, and accurate analytical tool for the oil analysis program.

CHAPTER IX
RECOMMENDATIONS

To further improve the analytical performance and manufacturability of the PWMA, the following recommendations are suggested.

a. Use 220 V ac only for the power source to eliminate the complication of high current switching between 220 V and 110 V. This would reduce the weight of the instrument as well as the cost of it.

b. Select either water or air for cooling the graphite furnace to facilitate the design improvement of cooling efficiency. Since the graphite furnace assembly is a modular design, the water or air cooling mode can be interchanged by replacing the furnace assembly and changing the cooling time of the atomization cycle.

c. Reassess the working ranges required for aircraft oil analysis so that the calibration of the instrument can be focused on commonly used ranges, thus improving the accuracy. If the concentration of a certain metal is high, the sample can be diluted with MIL-L-7808 blank oil and re-analyzed. The tradeoff would be the instrument's accuracy versus operational convenience and wider applicability.

d. Analyze silicon in a separate run, since silicon analysis is not presently required for most of the aircraft. This will allow the optimization of the atomization cycle, thus improving the performance of the other elements. Detail is discussed in Paragraph 7.4.

e. Reduce the operating temperature specification from -18 to 57 degrees centigrade to 0 to 50 degrade. This temperature reduction will simplify the component selection constraint, as discussed in Paragraphs 4.3.1 and 4.3.2, thus reducing the manufacturing cost.

f. Other areas where improvements can easily be made are discussed in Paragraph 7.6.

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APPENDIX A

PWMA PROTOTYPE TEST DATA

APPENDIX A

Test data of the prototypes are compiled in Tables 4 through 15. The following paragraphs summarize how the data were obtained.

1. Repeatability data were obtained by taking the standard deviation of results from 15 replicate samples.

2. Accuracy, dynamic range, detectability, and sample composition data were obtained by averaging the results from 5 replicate samples; particle size test data were the average values of 3 replicate samples.

3. All the test samples are prepared from the CONOSTAN metallo-organic standards except for the particle size test.

4. Samples for particle size test were supplied by Aero Propulsion Laboratory in July, 1983.

5. Samples for sample composition test were supplied by JOAP-TSC in August, 1984.

6. Data of column A of S/N 001 were tested using 220 V input power.

7. Data of column B of S/N 001 were tested using 110 V input power after completing all the environmental tests.

8. Data of S/N 002 through S/N 006 were tested using 208 input power.

9. Data of Tables 9 through 11 were tested with reduced dynamic range (1-25 ppm) of Al and Mg.

10. All the data were taken by W. Niu, except data from units S/N 002 and S/N 006.

11. All the numbers are expressed in parts per million.

TABLE 4. Repeatability Test of 10% 7808 Sample (in ppm)*

	S/N 001 A	S/N 001 B	S/N 002	S/N 003	S/N 004	S/N 005	S/N 006
Ag	0	0.26	0	0	0	0.26	0.26
Al	0.65	0.56	1.9	0.51	2.92	5.07	0.7**
Cr	0	0	0.26	0	0	0	0
Cu	0	0.74	0.7	0.46	0.38	1.1	0.84
Fe	0.64	0.74	0.83	0	0.74	0.51	1.45
Mg	0.51	0.7	0.26	0.41	0.49	0.26	0.39**
Ni	0.46	0.4	0.51	0.26	0.51	0.46	0.36
Si	1.2	1.6	1.06	0.46	0.82	1.67	0.36
Ti	0.99	0.38	0.74	0.41	0.52	0.35	0.39

*The repeatability readings are calculations of standard deviations of 15 successive measurements of the same sample.

**With reduced dynamic range (1-25 ppm)

TABLE 5. Repeatability Test of 50% 7808 Sample (in ppm)

	S/N 001 A	S/N 001 B	S/N 002	S/N 003	S/N 004	S/N 005 A	S/N 005 B	S/N 006
Ag	0	0.64	0.41	0.52	0.41	0.46	0	0.5
Al	4.5	2.5	1.8	17.6	9.7	6.85	1.8*	1.96*
Cr	0.46	0.5	0.26	0.35	0.86	0	0.49	0.25
Cu	0.67	0.77	1.07	1.08	1.55	0.99	1.15	1.75
Fe	2.2	1.6	2.2	1.99	5.05	1.67	1.7	3.53
Mg	5.3	7.8	3.92	7.23	17.7	7.08	1.45*	0.97*
Ni	0.64	0.82	0.46	0.46	0.64	0.52	0.4	0.62
Si	2.1	2.0	1.34	1.37	2.29	3.08	0.67	2.26
Ti	1.9	0.95	0.74	0.83	0.9	0.97	0.82	0.88

*With reduced dynamic range (1-25 ppm)

TABLE 6. Accuracy Test of 10% 7808 Sample (in ppm)

	Calibration* Standard	Measured Concentration* S/N 001 A	S/N 001 B	S/N 002	S/N 003	S/N 004	S/N 005
Ag	1	1	0	1	2	1	1.8
Al	5	6	6.8	6	3.4	12.6	14.8
Cr	1	1	1	1	1	1	1
Cu	4	4	2	4.6	5.8	4	5.4
Fe	10	12.6	9.4	12.2	12.2	9	10.2
Mg	5	3.4	3	5	5	4.8	4
Ni	3	5.4	2.8	3	3	3	3
Si	2	2.4	2.4	3	2.2	1.8	2.4
Ti	2	3	3	2	1.6	2.2	2

*Gravimetrically prepared.

*Average of 5 successive measurements of the same sample.

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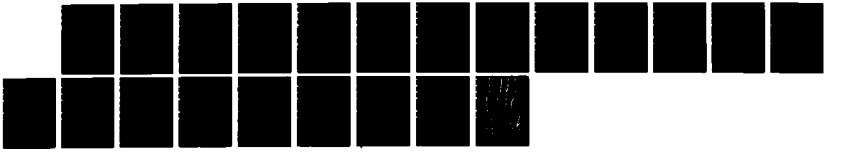

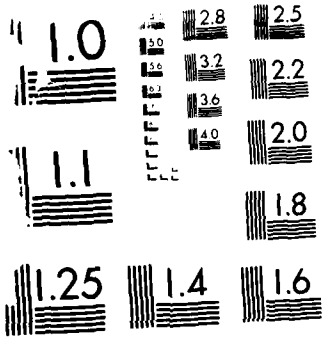

MICROCOPY RESOLUTION TEST CHART

TABLE 7. Accuracy Test of 40% 7808 Sample (in ppm)

	Calibration Standard	Measured Concentration					
		S/N 001 A	S/N 001 B	S/N 002	S/N 003	S/N 004	S/N 005
Ag	4	3.6	5	4	4.4	4.6	5
Al	20	14.4	14.8	22.4	14.4	30.6	34.8
Cr	4	4.2	4	4	4.2	4.4	4
Cu	16	14.6	16	17	16.6	16.4	17.2
Fe	40	36	42	40.2	45	41	39.6
Mg	20	9	14.6	22.4	15.8	19.2	13.8
Ni	12	9.8	12	12	12	12.8	11.6
Si	8	6.2	6.2	8.2	6.8	10.6	9.4
Ti	8	10.8	9.4	9.4	8.4	8.2	7.4

TABLE 8. Accuracy Test of 70% 7808 Sample (in ppm)

	Calibration Standard	Measured Concentration					
		S/N 001		S/N 002	S/N 003	S/N 004	S/N 005
		A	B				
Ag	7	7	7.2	7.8	8	7.8	8.4
Al	35	32.4	26.4	32.4	17.6	57.4	39
Cr	7	6.4	7.2	6.4	7.6	7	6.8
Cu	28	24.8	27.4	26.6	29	27.6	29.4
Fe	70	73.6	76.6	66.8	74.8	72	69.6
Mg	35	16.2	38.2	29.2	29.2	40	14.4
Ni	21	21.6	21.6	22.4	21.2	21.6	20.4
Si	14	17.6	9	10	10.4	16.5	12.4
Ti	14	20.6	15.2	15.8	15.2	15.6	14.8

TABLE 9. Accuracy Test of 10% 7808 Sample With Reduced Dynamic Range of Al and Mg (in ppm)

	Calibration Standard	Measured Concentration			
		S/N 003	S/N 004	S/N 005	S/N 006
Ag	1	1	1	1	1
Al	2.5	2.6	2.2	1.8	2.2
Cr	1	1	1	1	1
Cu	4	5	3.4	4.4	3.8
Fe	10	13.6	8.2	9	8
Mg	2.5	2	2	2	2
Ni	3	3	2.2	3	2.2
Si	2	5	1	1	.6
Ti	2	2	2.6	3	2.2

TABLE 10. Accuracy Test of 40% 7808 Sample With Reduced Dynamic Range of Al and Mg (in ppm)

	Calibration Standard	Measured Concentration			
		S/N 003	S/N 004	S/N 005	S/N 006
Ag	4	4	4	4	4
Al	10	10.8	11.5	7.4	10.8
Cr	4	4	4	4.2	4
Cu	16	17.6	16	16.2	15.4
Fe	40	42	39.4	38.6	42.2
Mg	10	8	9.2	8.4	14.4
Ni	12	12.2	12.2	12	12.8
Si	8	11.6	8.6	7.4	9.6
Ti	8	8	9	9	9.2

TABLE 11. Accuracy Test of 70% 7808 Sample With Reduced Dynamic Range of Al and Mg (in ppm)

	Calibration Standard	Measured Concentration S/N 003	S/N 004	S/N 005	S/N 006
Ag	7	7.8	7.4	8.2	6
Al	17.5	27	17.4	11	18.8
Cr	7	7.4	6.8	7	7.4
Cu	28	26.6	27.8	28.2	25.6
Fe	70	66.6	69.2	69	71
Mg	17.5	16.2	16.4	16.2	20.4
Ni	21	21.8	21.8	21.6	23.4
Si	14	16	14.8	15.6	15.8
Ti	14	14	14.4	14.4	16.4

TABLE 12. Dynamic Range Test of 90% and 100% 7808 Samples (in ppm)

	100%		90%	
	Calibration Standard	Measured Concentration (S/N 001)	Calibration Standard	Measured Concentration (S/N 001)
Ag	10	10.2	9	8.6
Al	50	49.2	45	40
Cr	10	8	9	7.8
Cu	40	37.8	36	32.8
Fe	100	97.8	90	89.8
Mg	50	27	45	19.6
Ni	30	29	27	27.6
Si	20	30.4	18	25.2
Ti	20	25.2	18	24

TABLE 13. Detectability Test of 1 PPM MIL-L-7808 Sample (in ppm)

	Calibration Standard	Measured Concentration* S/N 001 A	S/N 001 B	S/N 002	S/N 003	S/N 004	S/N 005
Ag	1	1	0	0.8	1	1	1
Al	1	0.8	0.6	1	0.6	1	1.4
Cr	1	1	2	1	1	1	1
Cu	1	0	0	1.2	1.2	1	1.4
Fe	1	2	1	1	1	1	1.2
Mg	1	1	1	0.6	0	1	0
Ni	1	3	2	1	1	1	1
Si	1	0	0	0.4	0.8	0.2	0.6
Ti	1	1.4	0	1	1.2	1.2	1

*Difference between the average of 5 successive measurements of 1 ppm sample and the average of 5 successive measurements of 0 ppm sample.

TABLE 14. Particle Size Test Using 10-20 Micrometer Particles Dissolved in 7808 Oil (in ppm)

	Calibration* Standard	Measured Concentration (S/N 001)
Ag	10	4
Al	50	20
Cr	10	6
Cu	40	5
Fe	100	56
Mg	50	21
Ni	30	12
Si	20	35
Ti	20	22

*Supplied by Aero Propulsion Laboratory

TABLE 15. Sample Composition Test Using 6082 and 23699 Oil Samples (in ppm)

	Calibration* Standard	Measured Concentration (S/N 003)		Calibration* Standard	Measured Concentration (S/N 003)		Calibration* Standard	Measured Concentration (S/N 003)	
		23699	6082		23699	6082		23699	6082
Ag	2	2	1	5	5.6	2.4	10	11	6
Al	10	14	9.4	25	51.2	18.6	50	45.8	24.7
Cr	2	2	1	5	4.8	2.8	10	9.2	6.7
Cu	8	7.6	4.8	20	18.4	10.4	40	36	21
Fe	20	20.4	13.6	50	42.2	20.4	100	95.2	41.7
Mg	20	8.8	4.6	25	33.4	19.6	50	46.4	33
Ni	6	7	3.8	25	14.6	8.2	30	30.2	16.2
Si	4	3.4	1.8	10	7.6	3	20	16.6	9
Ti	4	5.2	3.4	10	11.8	8.4	20	19.2	16.5

*Supplied by JOAP-TSC

APPENDIX B

FIELD TEST PLAN

PWMA Field Evaluation Test Plan

I. Scope

This test plan serves as a preliminary guideline for the field evaluation of the PWMA. A formal test procedure will be issued by the Aero Propulsion Laboratory, AFWAL, WPAFB.

II. Purpose

The PWMA is primarily designed for the Air Force to support oil analysis during deployment. Field test is to evaluate the feasibility of using the PWMA for this purpose. Parameters to be evaluated during the field test are described below.

(A) Analytical Parameters

1. Test the graphite tube variation effect on analytical data.

2. Evaluate the effectiveness of Reslope.

3. Evaluate the graphite tube life.

4. Evaluate the variations among different units.

5. Test the stability of Argon regulator.

6. Test environmental compatibility.

7. Identify optimum calibration functions.

(B) Statistical Analyses

1. Provide measures of accuracy and repeatability for different types of samples as a function of concentration level.

2. Measure variability due to differences in operators and test if this variability is significant.

3. Measure variability due to days and test for significance.

4. Test for calibration drift within a day.

5. If appropriate data is available measure the effect of differences in environmental factors.

III. Test Plan

The test program will be divided into two phases, each using the same data sheets. Phase I includes the test of 6 graphite tubes (approximately 960 samples) in fixed laboratory environments. Phase II includes the test of 6 additional graphite tubes in different environments with emphasis on mobility. The test sequence of each tube shall follow the PWMA Field Test Burn Sequence shown in Section VI. All the samples analyzed by PWMA shall be analyzed by the AE instrument; the AE instrument shall be calibrated according to its own procedure.

IV. Definitions

All the terms referred to in the Burn Sequence are defined below:

(A) Tube Condition. Tube condition is required for each new tube used; however, no data will be recorded on tube condition mode.

(B) Auto Zero (AZ). A blank MIL-L-7808 oil sample will be analyzed.

(C) CAL I, CAL II, CAL III. Three calibration samples prepared in MIL-L-7808 oil contain 20%, 50%, and 100% of full scale for all nine wear metals. Perkin-Elmer will provide these samples.

(D) Verification Samples. Three verification samples prepared in MIL-L-7808 oil contain 10%, 40%, and 70% of full scale for all nine metals. Perkin-Elmer will provide these samples.

(E) Correlation Samples. These are used jet engine oil samples. Each sample shall contain a minimum of 7 wear metals (preferably 9). JOAP-TSC shall provide 9 sets of correlation samples delivered to all five evaluation sites. Each sample bottle shall contain no less than 200 cc of oil.

(F) Random Samples. These are routine daily samples obtained at each evaluation site.

(G) Reslope. A 50% of full scale sample will be used for reslope.

(H) Calibration Check Samples. These are the 20%, 50%, and 100% of full scale samples analyzed in the Analysis mode.

(I) AZ failure. In some situations, the tube will produce erratic results with blank oil sample. If these situations occur, e.g., AZ failed twice successively, this tube shall not be used.

(J) Calibration Failure. If the calibration failed twice in a row (with no obvious operator error), the tube shall be replaced.

(K) Blank. No sample is injected, only the START button is activated.

V. Operational Notes

This section highlights some important notes for operating the PWMA.

(A) Sample Introduction

Sample introduction is the key to obtain repeatable results for the PWMA. It is important that the operator develop a consistent way to place the sample tip into the aperture of the graphite tube. The

front end of the sample tip shall not touch any surface to avoid loss of sample.

(B) Sample Tip

When picking the sample from the container, only the front end of the tip needs to be immersed into the oil. It is recommended that the tip be dipped into the oil as little as practical to provide a "clean" sample pick up. If the tip body is contaminated with oil, a Kim-Wipe can be used to clean off the excess oil. However, care has to be exercised not to wipe the front end of the tip.

(C) Sample Handling

The lid of the sample bottle can be used to hold the sample. However, it is recommended that the oil left in the lid be discarded after use to avoid contamination. Also, a small bottle shall be used for daily sampling. After the sample is used up, refill the small bottle from large one.

(D) Sample Gun

When the Argon supply is first turned on the trigger of the sample gun should be pushed to release the pressure build-up due to initial gas surge. During the sample injection, the trigger should only be pushed once. If the gun is accidentally pushed more than once, make a note on the data sheet for that sample.

(E) Sample Introduction

Right after the sample introduction, the START button should be pushed. Do not leave the sample in the tube for extended periods, otherwise, the sample tends to soak into the tube. If the sample is accidentally injected into the tube before the ready light is on, make a note on the data sheet for that sample.

(F) Calibration

In order to provide a more accurate result, two point average calibration will be used for the field test, i.e., two CAL I samples will be run at CAL I position, two CAL II samples will be run at CAL II position, and two CAL III samples will be run at CAL III position. For each calibration run, the absorbance data will be printed out. The PWMA will average the two CAL I data, two CAL II data, and two CAL III data and store them as calibration points, but the averaged value will not be printed out.

Similar methods are applied to reslope. For each reslope run, the absorbance data will be printed out. The PWMA will average the two reslope data and calculate the reslope ratio, but the ratio will not be printed out.

(G) Set-up

When using the set-up mode to read the electrometer output, if the system re-boots itself, push the START button again to re-enter the set-up operation. If the system locks in a certain mode, turn off the power and then turn power back on, push the START button again to enter the set-up operation.

(H) Tube Burn

If the exterior of the graphite tube shows a burn mark (looks like a cut) before reaching the end of the tube life, it is an indication that the Argon gas sheath has been penetrated. If this happens persistently, call for assistance.

VI. PWMA Field Test Burn Sequence

First Day

1. Tube Condition
2. Auto Zero - Operate in AZ mode. If the AZ failed, redo the AZ and number the run as 2A. If the AZ failed twice in a row, replace the tube.
3. CAL Ia - Operate in CAL I mode.
4. CAL Ib - Operate in CAL I mode.
5. CAL IIa - Operate in CAL II mode.
6. CAL IIb - Operate in CAL II mode.
7. CAL IIIa - Operate in CAL III mode.
8. CAL IIIb - Operate in CAL III mode. If the calibration failed, redo the calibration and number the calibration runs as 3A, ..., 8A, accordingly.
9. Blank - Run a burn with no sample; operate in Analysis mode. From no on, all the samples will be run in Analysis mode except Reslope.
10. 10% sample
11. 40% sample
12. 70% sample
13. Blank

14-18. Correlation sample #1 - Repeat the same sample five times, this procedure applies for all the correlation samples.

19-23. Correlation sample #2

24-28. Correlation sample #3

29. Blank

30-37. Random Samples - This can be real engine oil samples. If there are not enough real engine oil samples, repeat one sample as many times as necessary. (8 samples total.)

38. 10% sample
39. 40% sample
40. 70% sample

Second Day

41. Blank
42. Reslope A - Operate in RSLP mode. If the reslope A failed, disregard and continue the sequence.
43. Reslope B - Operate in RSLP mode. If the reslope B failed, disregard and continue the sequence.
44. 10% sample
45. 40% sample
46. 70% sample
47-51. Correlation sample #4
52-56. Correlation sample #5
57. Blank
58-63. Random samples (6 samples total)
64. CAL I check sample - Operate in Analysis mode.
65. CAL II check sample - Operate in Analysis mode.
66. CAL III check sample - Operate in Analysis mode.
67. Blank
68-77. Random samples (10 samples total)
78. 10% sample
79. 40% sample
80. 70% sample

Third Day

81. Blank
82. CAL Ia.
83. CAL Ib.
84. CAL IIa.
85. CAL IIb.
86. CAL IIIa.
87. CAL IIIb.
88. Blank
89. 10% sample
90. 40% sample
91. 70% sample

92-96. Correlation sample #6

97-101. Correlation sample #7

102. Blank

103-117. Random samples (15 samples total)

118. 10% sample

119. 40% sample

120. 70% sample

Fourth Day

121. Blank

122. Reslope A

123. Reslope B

124. 10% sample

125. 40% sample

126. 70% sample

127-131. Correlation sample #8

132-136. Correlation sample #9

137. Blank

138-157. Random samples (20 samples total)

158. Cal I check sample

159. CAL II check sample

160. CAL III check sample

APPENDIX C

LIST OF ABBREVIATIONS

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Ag	Silver
Al	Aluminum
Cr	Chromium
Cu	Copper
Fe	Iron
Mg	Magnesium
Ni	Nickel
Si	Silicon
Ti	Titanium
Amp	Ampere
AA	Atomic Absorption
A/D	Analog to Digital
ASCR	Asymmetrical Silicon Controlled Rectifier
°C	Centigrade
CFM	Cubic Feet Per Minute
DFM	Design File Memo
DoD	Department of Defense
EPROM	Electrical Programmable Read Only Memory
FAA	Flame Atomic Absorption
g	Gravity
GFPS	Graphite Furnace Power Supply
HCL	Hollow Cathode Lamp
He-Ne	Helium-Neon
HGA	Heated Graphite Furnace
Hz	Cycles Per Second
I/O	Input/Output
JOAP	Joint Oil Analysis Program
kHz	Kilohertz
MPU	Microprocessor Unit
ml/min	Milliliters Per Minute
µs	Microsecond
PMT	Photomultiplier Tube
ppm	Parts per Million
PWMA	Portable Wear Metal Analyzer
psi	Pounds Per Square Inch
psig	Pounds Per Square Inch Gage
%	Percent
RAM	Random Access Memory
ROM	Read Only Memory
SCR	Silicon Controlled Rectifier
sec	Second
SOAP	Spectrometric Oil Analysis Program
USAF	United States Air Force
VAC	Volt Alternating Current

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